Hyperfine fields and magnetic moments in intermetallic $Sc_{1-x}Zr_xFe_2$ ($0\leqslant x\leqslant 1$) Laves cubic compounds

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(Submitted 22 November 1988)
Zh. Eksp. Teor. Fiz. **95**, 2079–2089 (June 1989)

The NMR method was used to determine the hyperfine fields at the ^{45}Sc, ^{57}Fe, and ^{91}Zr nuclei in $Sc_{1-x}Zr_xFe_2$ ($0\leqslant x\leqslant 1$) Laves cubic compounds, as well as at ^{27}Al impurity nuclei replacing iron atoms over the entire concentration range. Estimates were obtained of the contributions made to the hyperfine field at ^{57}Fe by the local magnetic moment of the iron atoms $H_{\rm loc}$(Fe) and of the magnetic moments of the nearest spheres $H_{\rm ind}$(Fe). The values of $H_{\rm loc}$(Fe) were used to estimate the magnetic moments of the iron atoms μ(Fe) and the magnetic moment μ_f per formula unit of the compound was employed in finding the magnetic moments μ(Sc, Zr) at the states occupied by scandium and zirconium ions. In the range of compositions $0\leqslant x\leqslant 0.5$ the magnetic moments μ(Fe) increased from $(1.61\pm 0.03)\mu_B$ to $(1.83\pm 0.03)\mu_B$, whereas μ(Sc, Zr) varied from $(-1.02\pm 0.05)\mu_B$ to $(-0.50\pm 0.05)\mu_B$. For compositions in the $0.5\leqslant x\leqslant 1$ range the values of μ(Fe) and μ(Sc, Zr) remained constant within the limits of experimental error. The hyperfine field at ^{45}Sc ranged from -103.4 to -63.8 kOe when the zirconium concentration was increased in the range $0\leqslant x\leqslant 1$, whereas the hyperfine field at ^{91}Zr varied from -143.7 to -128.7 kOe for $0.8\leqslant x\leqslant 1$. The composition dependence of the hyperfine field H(Sc) at ^{45}Sc was correlated with the composition dependence μ(Sc, Zr) in the range $0\leqslant x\leqslant 0.5$. The magnetic moments at the atoms of iron, scandium, and zirconium, and their composition dependences were explained using calculations of the electron structure of the cubic Laves phases, and by hybridization of the 3*d* band of iron with the 4*d* and 3*d* bands of zirconium and scandium.

1. INTRODUCTION

Hyperfine interaction methods must be included among the technique for estimating local magnetic moments in ferromagnets. The difficulties encountered in estimating the magnetic moments from the hyperfine fields are due to the fact that in the case of many specific alloys there is no clear way of finding quantitatively the contributions made to the hyperfine fields at the nuclei of atoms in the alloys. Determination of such contributions relies largely on the values of the magnetic moments of atoms in an alloy.

It is frequently assumed that in intermetallic Laves compounds based on AFe_2 (A = Zr, Sc, Y, etc.) the A atoms have no magnetic moment, so that the hyperfine fields at the nuclei of the A atoms do not include a contribution from the polarization of the inner *s* electrons and outer itinerant collective-state electrons due to the magnetic moment of the A atoms. This has resulted in errors of interpretation of the nature of the hyperfine fields of these atoms and in estimates of the various contributions to the hyperfine fields, and has led to incorrect values of the magnetic moments of the iron atoms in such compounds deduced from the data on the hyperfine field at ^{57}Fe and the average magnetization of an alloy (or the magnetic moment per formula unit).

Recent calculations of the electron structure of intermetallic $ZrFe_2$ (Refs. 1 and 2) and $ScFe_2$ (hexagonal) compounds have shown that the atoms of zirconium and scandium have magnetic moments $\mu(\mathrm{Zr}) = -0.56\mu_B$ and $\mu(\mathrm{Sc}) = -0.52\mu_B$. The data on the hyperfine field at ^{91}Zr in $ZrFe_2$, containing 3*d* impurity atoms at the iron atom sites, are used in Ref. 3 to separate the contributions made to the hyperfine field at ^{91}Zr by the magnetic moments of the atoms in the nearest spheres (representing a large negative contribution) and by the magnetic moments of the atoms of zirconium (large positive contribution). An estimate of μ(Zr) from the hyperfine field at ^{91}Zr gives $\mu(\mathrm{Zr}) = (-0.5\pm 0.1)\mu_B$, which is in good agreement with calculations of μ(Zr) based on the electron structure. Some published experimental data on the hyperfine fields at the A and iron atoms in AFe_2 Laves compounds as well as calculations of the hyperfine fields, μ(A), and μ(Fe) from the electron structure of Laves phases with the cubic and hexagonal structures have shown that the existing ideas on the nature of the hyperfine fields and on the values of the magnetic moments at the A and Fe atoms in Laves phases need some refinement. Our aim was to measure the hyperfine fields at the ^{45}Sc, ^{57}Fe, and ^{91}Zr nuclei in $Sc_{1-x}Zr_xFe_2$ Laves phases in a wide range of compositions, to estimate the contributions made to the hyperfine fields of ^{57}Fe, and to find the values of the magnetic moments of the iron atoms as well as to determine whether the states of the scandium and zirconium atoms in the lattice have magnetic moments.

2. STRUCTURE AND MAGNETIC PROPERTIES OF INVESTIGATED ALLOYS

We investigated $Sc_{1-x}Zr_xFe_2$ Laves alloys with the cubic structure of $MgCu_2$ (A15). It is known that in the $MgCu_2$ structure the atoms of scandium (or zirconium) form an fcc lattice with octants containing alternately scandium (or zirconium) atoms or regular tetrahedra of iron atoms.[4] When the concentrations of scandium and zirconium in the alloys of intermediate compositions are altered, the scandium and zirconium atoms become mutually transposed and this is probably a random process. There is no published information on the magnetic properties of

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$Sc_{1-x}Zr_xFe_2$ Laves compounds. Extensive investigations have, however, been made of the intermetallic compound $ZrFe_2$. It is known that $ZrFe_2$ is a ferromagnet with a Curie temperature of 630 K and an average magnetic moment of $1.63\mu_B$ per iron atom[5] (it was assumed in Ref. 5 that zirconium atoms have no magnetic moment). The lattice parameter of this intermetallic alloy is $a = 7.07$ Å. Mössbauer investigations of $ZrFe_2$ (Ref. 6) have shown that the hyperfine fields at the ^{57}Fe nuclei have isotropic and anisotropic components. The hyperfine fields at the ^{91}Zr nuclei have been determined by the nuclear magnetic resonance (NMR) method on several occasions (see, for example, Refs. 7 and 8). The NMR spectrum of ^{91}Zr consists of the main line at 50 MHz and several weak lines at higher frequencies and the latter lines are observed because the atoms of iron occupy the zirconium atom sites.

An NMR investigation of $ScFe_2$ was reported recently.[9] It follows from the published data that the compound $ScFe_2$ can exist in three modifications: 1) cubic with the $MgCu_2$ structure[10]; 2) hexagonal with the $MgNi_2$ structure[11]; 3) hexagonal with the $MgZr_2$ structure.[12] It is shown in Ref. 9 that the structure of $ScFe_2$ is very sensitive to the iron (or scandium) concentration in the alloy. The $ScFe_2$ alloy with cubic structure can be obtained reproducibly with the stoichiometric composition or with a small excess of scandium. In the presence of excess iron the structure of $ScFe_2$ becomes hexagonal of the $MgNi_2$ type, whereas a considerable excess of scandium leads to the hexagonal modification with the $MgZn_2$ structure (containing an admixture of the $ScFe_3$ phase).[10] The lattice parameter a of $ScFe_2$ with the cubic structure has been determined in several investigations; its values are reported as 7.09 Å in Ref. 10 and 7.047 Å in Ref. 9. The differences between the values of a reported for the cubic phase of $ScFe_2$ are probably due to deviations of the concentrations of the components of this alloy from stoichiometry. The NMR method can be used to distinguish reliably the $MgCu_2$ from the $MgNi_2$ structure on the basis of the number of the NMR lines of the ^{57}Fe and ^{45}Sc nuclei which correspond to the number of crystallographically inequivalent states of the iron and scandium atoms (one state of iron and one state of scandium in the case of the $MgCu_2$ structure, but three states of iron and two states of scandium in the case of the $MgNi_2$ structure). The hyperfine fields at the ^{45}Sc and ^{57}Fe nuclei in $ScFe_2$ with the $MgCu_2$ structure at 4.2 K have been determined in Ref. 9. For the ^{45}Sc nuclei we have $H(Sc) = -101$ kOe, whereas for the ^{57}Fe nuclei the field is $H(Fe) = -200$ kOe (deduced ignoring the Lorentz field).

3. SAMPLES AND MEASUREMENT METHOD

The investigated alloys were prepared from mixtures of high-purity metals in an argon atmosphere using an arc furnace with a water-cooled copper stage. The investigation was carried out on 16 single-phase $Sc_{1-x}Zr_xFe_2$ alloys with $0 \leqslant x \leqslant 1$ and 7 single-phase alloys of the compositions $Sc_{1-x}Zr_xFe_{1.97}Al_{0.03}$ as well as $ScFe_{1.95}Al_{0.05}$, $ZrFe_{1.98}Al_{0.02}$ and $ZrFe_{1.95}Al_{0.05}$. Samples with the exact stoichiometric composition were obtained provided the original charge had an excess of scandium and aluminum amounting to 5–10%. The resultant ingots were remelted several times. The samples used were powders with grains of $\leqslant 70\,\mu$m size. They were prepared both from ingots subjected to homogenization for 50 h at 750 °C and from ingots cooled directly in the arc furnace. Annealing had practically no influence on the measured parameters. The crystal structure of the alloys was determined by x-ray diffraction. We carried out the investigation selecting alloys with the cubic $MgCu_2$ structure. Chemical and plasma-spectroscopic analyses demonstrated that the alloys had the expected compositions. In the case of alloys with compositions in the range $0 \leqslant x \leqslant 0.15$ the second phase with the $MgNi_2$ structure could be present in amounts less than 5% (which was the error in x-ray structure analysis). The saturation magnetization σ was measured at 77 K using a vibration magnetometer and compacted powder samples. The relative error in the determination of σ obtained for three or four samples made of compacted powders amounted to 3–5%.

Pulsed NMR spectra were recorded point-by-point at frequencies in the range 10–150 MHz at 4.2 K. The experimental conditions were such that the amplitude of the echo signal A_e varied with the measurement frequency f as $A_e \propto f^2$; the NMR spectra of ^{57}Fe and ^{27}Al were in the range 20–34 MHz, the spectrum of ^{91}Zr was in the range 45–62 MHz, and that of ^{45}Sc was at 60–115 MHz.

The addition of $\gtrsim 2$ at.% of Zr, Y, or Gd to $ScFe_2$ stabilized the cubic phase of $MgCu_2$.

4. EXPERIMENTAL RESULTS

Figure 1a shows the composition dependence of the room-temperature lattice parameter a of the cubic $Sc_{1-x}Zr_xFe_2$ $(0 \leqslant x \leqslant 1)$ Laves phases. The positions of the x-ray lines and their intensities corresponded more closely to the cubic structure of the $MgCu_2$ type than to the hexagonal structures of the $MgZn_2$ and $MgNi_2$ types. The NMR spectra of the ^{57}Fe, ^{45}Sc, and ^{91}Zr nuclei also confirmed the cubic $MgCu_2$ structure of these alloys. The lattice parameter a was deduced from the maximum and from the center of gravity of the (440) reflection. The error in the determination of a was 0.0025 Å. Figure 1(b) gives the composition dependence of the saturation magnetization σ, whereas Fig. 1(c) gives the corresponding dependence of the magnetic moment μ_f per formula unit. Since the Curie temperatures of $ScFe_2$ and $ZrFe_2$ were fairly high,[8,9] the values of μ_f at 77 K were used to estimate the magnetic moments of the atoms in these alloys at 4.2 K. It is clear from Fig. 1 that the replace-

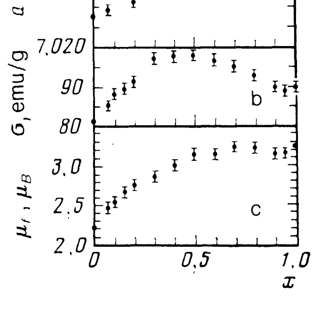

FIG. 1. Composition dependences of: a) lattice parameter a at 293 K; b) saturation magnetization σ at 77 K; c) magnetic moment per formula unit μ_f at 77 K.

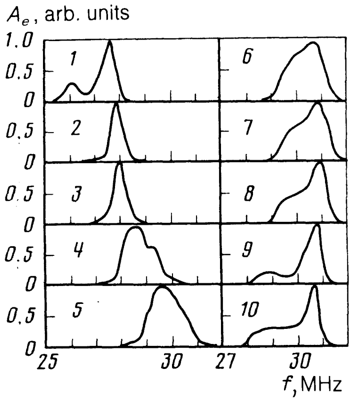

FIG. 2. Nuclear magnetic resonance spectra of ^{57}Fe in $Sc_{1-x}Zr_xFe_2$ alloys with $x = 0$ (1), 0.05 (2), 0.1 (3), 0.3 (4), 0.4 (5), 0.5 (6), 0.6 (7), 0.7 (8), 0.9 (9), 0.95 (10).

ment of scandium atoms (with the $3d^14s^2$ electrons in the outer shell) by zirconium atoms (with the $4d^25s^2$ electrons in the same shell), i.e., the addition of one more d electron to the system, increased slightly the lattice parameter but enhanced considerably the magnetic moment per formula unit μ_f. The increments in a and μ_f were $\sim$0.43% and $\sim$41%.

Figure 2 shows the NMR spectra of ^{57}Fe in alloys of the $Sc_{1-x}Zr_xFe_2$ system. The resonance spectrum of $ZrFe_2$ agrees with the data reported in Refs. 7 and 8. The spectrum of ^{57}Fe in $ScFe_2$ consists of two allowed peaks with maxima at 26.1 and 27.6 MHz and intensity ratio 1:3. The addition of zirconium atoms in place of scandium suppresses the lf component in the NMR spectrum and shifts the main component toward higher frequencies. It is also clear from Fig. 2 that the shift of the main line toward higher frequencies involves appearance of a new component on the hf side of the spectrum. The NMR spectra of the alloys on the zirconium side also consist of two lines; in the case of $ZrFe_2$ one of the lines has a maximum at 29.0 MHz and the other at 30.6 MHz.

The splitting of the NMR lines of $ScFe_2$ is 1.5 MHz or 10.6 kOe, whereas in the case of $ZrFe_2$ it is 18 kOe, in agreement with Ref. 8.

The atoms of iron in the $MgCu_2$ lattice are in one crystallographic state and occupy sites in a regular tetrahedron.[4] In the case of YFe_2 and $ZrFe_2$, which also have the $MgCu_2$ structure, the direction of the easy axes is $\langle 111 \rangle$ at 4.2 K, which splits the NMR spectrum of ^{57}Fe into two lines with the intensity ratio 1:3. The lines in the spectrum of ^{57}Fe in $ScFe_2$ are characterized by a 1:3 ratio of the areas, so that the easy magnetization axis of $ScFe_2$ is $\langle 111 \rangle$ and the NMR splitting is due to the magnetic inequivalence of the atoms of iron in the $MgCu_2$ lattice.

It is clear from Fig. 2 that the replacement of scandium with zirconium in the (Sc, Zr)Fe_2 system gives rise to a single line in the NMR spectra of ^{57}Fe already for $x = 0.05$ and, consequently, it changes the direction of the easy axes from $\langle 111 \rangle$ to $\langle 001 \rangle$. However, when x is increased still further, the single line broadens because of the appearance of the hf component of the spectrum. If we assume that in the alloys containing $x = 0.4$–0.6 the easy axes switch to the $\langle 110 \rangle$ direction, then the NMR spectrum of ^{57}Fe in these alloys consists of two components with similar intensities, which additionally broaden the NMR spectrum and should probably be observed experimentally. A further increase in the zirconium content ($x > 0.6$) rotates the easy axes to the $\langle 111 \rangle$ direction. In the case of alloys close in composition to $ZrFe_2$ the easy axis is again directed along $\langle 111 \rangle$ and the NMR spectrum of ^{57}Fe is similar to the NMR spectra of ^{57}Fe in the cubic Laves phases based on iron and with two magnetically inequivalent iron states. It follows from Fig. 2 that the replacement of scandium with zirconium in the (Sc, Zr)Fe_2 system alters the directions of the easy magnetization axes from one alloy to another.

For example, in the $MgCu_2$-type lattices the easy magnetization axis coincides with the $\langle 111 \rangle$ direction and there are two angles between the electric field gradient axes which coincide with the symmetry-axes of the crystal lattice, on the one hand, and the directions of the magnetic moments, on the other. In this case, the atoms of iron become inequivalent in the magnetic sense. Three atoms of iron forming a tetrahedron are characterized by the angle $\theta = 70.5°$, whereas the remaining atom of iron in this tetrahedron has the angle $\theta = 0°$. The contributions of the dipole fields H_d made by these iron atoms to the NMR spectrum and to the hyperfine field at ^{57}Fe are different, and this difference is responsible for the hyperfine field anisotropy ΔH. A theoretical estimate of the contribution of the dipole fields to the hyperfine field at ^{57}Fe in the cubic system is calculated in Ref. 8, where its value is $\sim$6.5 kOe, which is close to ΔH for the compound YFe_2 in which case we have $\Delta H = 5$ kOe. The lattice parameter of YFe_2 is $a = 7.363$ Å and the magnetic moment of the iron atoms is $\mu(\text{Fe}) = 1.45\mu_B$/Fe atom[4] [on the assumption that $\mu(\text{Y}) = 0$]. In the case of $ZrFe_2$ we have $\Delta H = 18$ kOe; in this case the lattice parameter is $a = 7.065$ Å and $\mu(\text{Fe}) = 1.63\mu_B$/Fe atom [if $\mu(\text{Zr}) = 0$].[4] The high value of ΔH for $ZrFe_2$ is, according to the authors of Ref. 8, due to the pseudodipole hyperfine interactions. In the case of $ScFe_2$ with the $MgCu_2$-type lattice the corresponding values are $\Delta H = 10.6$ kOe, $a = 7.035$ Å, and $\mu(\text{Fe}) = 1.1\mu_B$/Fe atom [if $\mu(\text{Sc}) = 0$].

It follows that there is no correlation between the values of ΔH, the lattice parameters, and the magnetic moments of the iron atoms in the compounds YFe_2, $ZrFe_2$, and $ScFe_2$ which has the same crystal structure (it is assumed here that the magnetic moment of the A atoms in AFe_2 compounds are zero). Allowance for the magnetic moments of the scandium, zirconium, and yttrium atoms, and refinement of the magnetic moments of the iron atoms are likely to prove important for the understanding of the nature of the anisotropy of the hyperfine fields at the ^{57}Fe nuclei in Laves alloys.

Figure 3 shows the composition dependence of the average hyperfine fields H(Fe) at the ^{57}Fe nuclei (deduced from the centers of gravity of the NMR spectra) in $Fe_2Sc_{1-x}Zr_x$ compounds with the $MgCu_2$ structure. Replacement of scandium with zirconium increases almost linearly the value of H(Fe) from -199 to -222 kOe (including the Lorentz fields) in the range of compositions $0 \leqslant x \leqslant 0.5$ and gives rise to a maximum of H(Fe) at $x \approx 0.7$–0.8, but a further increase in the amount of zirconium in the alloys reduces H(Fe) slightly to $|H(\text{Fe})| = 220$ kOe. Replacing scandium with zirconium does not alter the immediate environment of the iron atoms: the scandium atoms are replaced with zirconium in the second coordination sphere of iron. However, transition from $ScFe_2$ to $Sc_{0.5}Zr_{0.5}Fe_2$ increases the hyperfine field

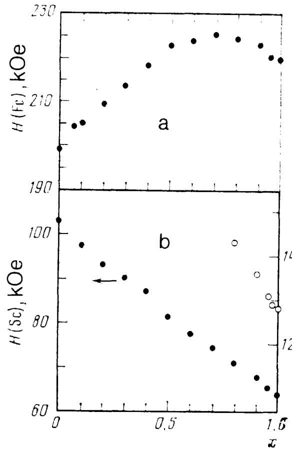

FIG. 3. Composition dependences of the average hyperfine fields at various nuclei: a) H(Fe) of ^{57}Fe; b) H(Sc) of ^{45}Sc (●) and H(Zr) of ^{91}Zr (○).

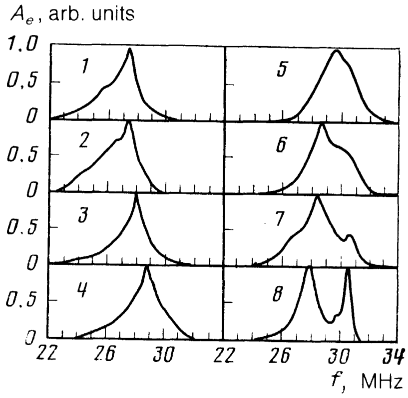

FIG. 4. Nuclear magnetic resonance spectra of the ^{27}Al impurity nuclei in $Sc_{1-x}Zr_xFe_{1.97}Al_{0.03}$ alloys with compositions $x = 0$ (1), 0.1 (2), 0.3 (3), 0.5 (4), 0.7 (5), 0.9 (6), and the spectra of $ZrAl_{0.03}Fe_{1.97}$ (7) and $ZrAl_{0.02}Fe_{1.98}$ (8) alloys.

H(Fe) by 23 kOe. In the range of compositions $0.5 \leqslant x \leqslant 1$ the replacement of scandium with zirconium, i.e., the appearance of three or four zirconium atoms instead of scandium in the second coordination sphere of iron, is sufficient to influence the hyperfine field H(Fe).

Figure 4 shows the NMR spectra of ^{27}Al for the impurity states of aluminum in $Sc_{1-x}Zr_xFe_{1.97}Al_{0.03}$ with $0 \leqslant x \leqslant 1$ and in $ZrFe_{1.98}Al_{0.02}$. In the case of the aluminum impurity in $ScFe_2$ the high-frequency part of the NMR spectrum of ^{27}Al is partly superimposed on the NMR spectrum of ^{57}Fe, whereas in the case of $ZrFe_2$ the spectrum of ^{27}Al and the main line of ^{57}Fe are well-resolved. The intensities of the NMR signals of ^{27}Al in alloys with the aluminum content $y = 0.03$ are 1.5–2 times greater than the intensity of the NMR signals of ^{57}Fe. These intensities are similar when the aluminum content is $y = 0.02$. We can see this clearly in the case of the spectra of ^{27}Al and ^{57}Fe in alloys with the aluminum concentrations $y = 0.02$ and 0.03. Table I demonstrates the composition dependence of the hyperfine field H(Al) of ^{27}Al deduced from the maximum of the NMR spectrum of ^{27}Al. The aluminum atoms occupy the iron atom sites in the $MgCu_2$-type lattice and have no magnetic moment. Therefore, H(Al) induced entirely by the field of the magnetic moments of the atoms in the first coordination sphere (6Fe) and by the magnetic moments of the atoms in the second coordination sphere [6(Zr + Sc)], i.e., by exactly the same atoms in the first and second coordination spheres as those influencing iron atoms.

Figure 5 shows the NMR spectra of the ^{45}Sc and ^{91}Zr nuclei for alloys with the compositions $x = 0.98$, $x = 0.95$, and $x = 0.90$. A single line at 50.0 MHz is usually reported[7,8] for $ZrFe_2$. The presence of 0.6 at.% of scandium ($Sc_{0.02}Zr_{0.98}Fe_2$) gives rise to additional lines at 52.2, 54.5, and 56.6 MHz, which are due to a resonance of the ^{91}Zr nuclei, and additional lines at 63.0, 65.4, 68.3, and 70.3 MHz which are due to the ^{45}Sc nuclei. The atoms of zirconium (and scandium) in $ZrFe_2$ containing scandium as an impurity have the first coordination sphere with 12Fe and the second coordination sphere with 4Zr [or 4(Zr + Sc)]. Further replacement of zirconium with scandium increases the intensities of these lines in the case of ^{45}Sc and ^{91}Zr and gives rise to additional allowed peaks. A comparison of the ratio of the intensities (areas) of the satellites and the main lines with the probabilities of a random distribution of zirconium and scandium atoms in the second coordination sphere of zirconium (or, correspondingly, of scandium) shows that the peaks at 50.0, 52.2, 54.5, 56.6, and 58.5 MHz for ^{91}Zr and the peaks at 63.0, 65.5, 68.3, 70.3, and 73.1 MHz for $0.9 \leqslant x \leqslant 1.0$ are due to the appearance of, respectively, zero, one, two, three, and four scandium atoms at the zirconium atom sites in the second coordination sphere of zirconium or scandium. It also follows from Fig. 5a that an increase in the scandium content in the range $0.9 \leqslant x \leqslant 1.0$ shifts the main satellite lines of ^{91}Zr and ^{45}Sc toward higher frequencies.

Figure 5 shows the NMR spectra of ^{45}Sc in $ScFe_2$ alloys containing zirconium atoms as an impurity in the amount $x = 0.07$. The spectra were recorded at 293 and 4.2 K. At

TABLE I.

x	$-H$(Al), kOe	$-H_{ind}$ (Fe), kOe	$-H_{loc}$ (Fe), kOe	μ(Fe) ±0,03, μ_B	μ(Sc, Zr) ±0,05, μ_B
0	24.4	54.5	144.5	1,61	−1.02
0.1	27.2	55.7	150.3	1.67	−0.83
0.3	28.0	57.4	156.6	1.74	−0.68
0.5	29.2	59.7	163,4	1.83	−0,54
0.7	28.5	58.3	168.3	1.87	−0.52
0.9	28.4	58.1	164.9	1.80	−0.51
1.0	27.8	57,0	164.8	1.83	−0.46

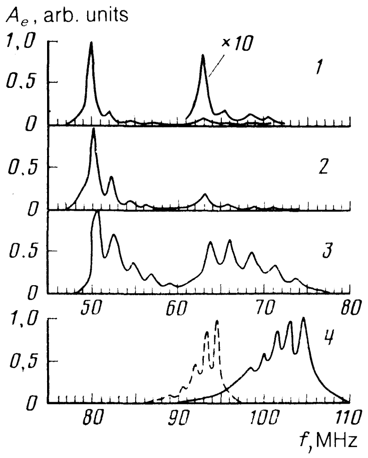

FIG. 5. Nuclear magnetic resonance spectra of ^{91}Zr and ^{45}Sc in $Sc_{1-x}Zr_xFe_2$ alloys with compositions $x = 0.98$ (1), 0.95 (2), 0.90 (3), and 0.07 (4) (the dashed curve was obtained at 293 K and the continuous one at 4.2 K).

293 K the spectra were resolved better and the ratio of the areas under the peaks agreed (within 10–15%) with the ratio of the probabilities of a random distribution of zirconium and scandium atoms in the second coordination sphere of scandium. Consequently, we can attribute these peaks to the states of scandium atoms as follows: the first coordination sphere contains 12Fe, whereas the second coordination sphere contains 4Sc (94.5 MHz), 3Sc + 1 Zr (93.3 MHz), 2Sc + 2Zr (92.0 MHz), 1Sc + 3Zr (90.6 MHz), or 4Zr (89.2 MHz). At 4.2 K the spectra are wider than at 293 K and they have additional lines. This effect is observed for the NMR spectra of ^{45}Sc in alloys up to $x = 0.15$. Probably small amounts of impurities of the second phase with the $MgNi_2$ structure ($\leqslant 5\%$), which are difficult to detect by x-ray diffraction at 293 K, are responsible for this influence on the NMR spectrum. Figure 6 shows the NMR spectra of ^{45}Sc for the other compositions of the alloys.

Figure 3(b) gives the average hyperfine fields H(Sc) and H(Zr), corresponding to the centers of gravity of the spectra, at the ^{45}Sc and ^{91}Zr nuclei in $Sc_{1-x}Zr_xFe_2$ alloys. An increase in the zirconium concentration reduces the average hyperfine fields $|H(\mathrm{Sc})|$ linearly from 103.4 to 63.8 kOe (i.e., by a factor of almost 1.8) in the range $0 \leqslant x \leqslant 1$, whereas $|H(\mathrm{Zr})|$ is reduced from 143.7 to 128.7 kOe in the range $0.8 \leqslant x \leqslant 1$. A comparison of Figs. 1 and 3 demonstrates the absence of a correlation between the composition dependences of the magnetic moment μ_f and of the hyperfine fields H(Sc) and H(Zr). In the range $0.5 \leqslant x \leqslant 1$ there is practically no change in μ_f, whereas H(Sc) and H(Zr) decrease considerably.

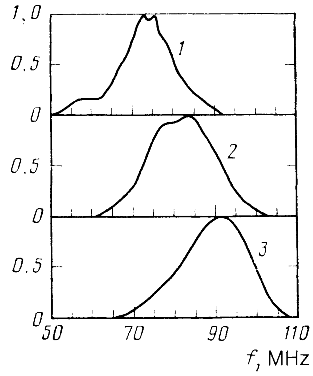

FIG. 6. Nuclear magnetic resonance spectra of ^{45}Sc in $Sc_{1-x}Zr_xFe_2$ alloys with $x = 0.3$ (1), 0.5 (2), and 0.7 (3).

5. DISCUSSION OF RESULTS

The hyperfine fields at the nuclei of the atoms with magnetic moments in Laves phases can be assumed to have the following components:

$$H = H_{\mathrm{res}} + H_s + H_{\mathrm{ind}}, \qquad (1)$$

where H_{res} is the residual contribution made to the hyperfine fields due to the polarization of the inner s electrons of an atom by the magnetic moment of the atom in question, H_s is the contribution made to the magnetic field as a result of the polarization of itinerant (collective-state) electrons by the magnetic moment of the same atom, and H_{ind} is the contribution made to the hyperfine field because of the polarization of itinerant electrons by the magnetic moments of the atoms in the nearest spheres. Since $H_{\mathrm{res}} = P_{\mathrm{res}}\mu$ and $H_s = P_s\mu$, it is usual to assume that $H_{\mathrm{res}} + H_s = H_{\mathrm{loc}} = P_{\mathrm{res}}\mu + P_s\mu = P\mu$, where P_{res}, P_s, and P are the polarization constants. If we consider only the contributions made to H_{ind} by the first and second coordination spheres, we find that Eq. (1) becomes

$$H = H_{\mathrm{loc}} + H_{\mathrm{ind}} = P\mu + H^{(1)}_{\mathrm{ind}} + H^{(2)}_{\mathrm{ind}}. \qquad (2)$$

The magnetic moments of the iron atoms μ(Fe) can be found from the experimental hyperfine fields H(Fe) using Eq. (2) if we can estimate the contribution made to H(Fe) by $H_{\mathrm{loc}}(\mathrm{Fe}) = P(\mathrm{Fe})\mu(\mathrm{Fe})$, since the constant P(Fe) is known and its value is $P(\mathrm{Fe}) = 90\ \mathrm{kOe}/\mu_B$ (Ref. 13). In estimating H_{ind}(Fe) in intermetallic $Sc_{1-x}Zr_xFe_2$ Laves compounds we shall use the scaling method developed in Ref. 13 for iron and its alloys containing impurities, of other atoms. According to Ref. 13, the contribution of H_{ind} to the hyperfine field at the nuclei of an impurity atom of B in iron (when B occupies the iron atom sites) can be estimated from H_{ind}(Fe) as follows:

$$H_{\mathrm{ind}}(\mathrm{Fe}) = A_s(\mathrm{Fe})np\mu, \quad H_{\mathrm{ind}}(\mathrm{B}) = A_s(\mathrm{B})np\mu, \qquad (3)$$

where A_s(Fe) and A_s(B) are the polarization constants of itinerant electrons for the iron and B atoms (they are independent of the alloy composition and are determined in Ref. 14), n is the number of the s electrons participating in the hyperfine interactions, p is the degree of polarization of these electrons, and μ is the magnetic moment (per atom) contributed by a specific coordination sphere or by the magnetic moments of the nearest spheres (depending on the model of the hyperfine field in each specific case). Clearly, in a given alloy the values of n, p, and μ are the same for an impurity atom occupying an iron atom site and for an atom of iron. Therefore, H_{ind}(B) and H_{ind}(Fe) deduced from Eq. (3) are mutually proportional.

The atoms of aluminum occupy the iron atom sites in the Laves compounds of iron and H_{ind}(Fe) and H(Al) are then due to the polarization of itinerant electrons by the magnetic moments in the first coordination sphere (6Fe) and in the second (6Sc, Zr) [if μ(Sc) and μ(Zr) have magnetic moments], i.e., H_{ind}(Fe) and H(Al) should be proportional to one another in accordance with Eq. (3). We solved the inverse problem for our Laves alloys by the scaling method: we used the measured values of H(Al) for the aluminum impurity atoms occupying the iron atom sites in the Laves phases and estimated H_{ind}(Fe) from

$$H_{\text{ind}}(\text{Fe}) = H(\text{Al})\{A_s(\text{Fe})/A_s(\text{Al})\}, \qquad (4)$$

where A_s(Fe) = 1780 kOe/1s and A_s(Al) = 789 kOe/1s (Ref. 14). Table I gives the values of H_{ind}(Fe) estimated from Eq. (4) using the experimental values of H(Al). The data on the hyperfine field H(Fe) of ^{57}Fe were substituted in Eq. (2) to obtain the contribution

$$H_{\text{loc}}(\text{Fe}) = P(\text{Fe})\,\mu(\text{Fe}) = H(\text{Fe}) - H_{\text{ind}}(\text{Fe}).$$

If we assume that $P(\text{Fe}) = 90$ kOe/μ_B, we can estimate the magnetic moment of the iron atoms μ(Fe) in the investigated Laves alloys. The values of μ(Fe) obtained in this way are listed in Table I. We can see that the magnetic moments of the iron atoms deduced from the hyperfine fields H(Fe) by the method described above increase from $1.61\mu_B$ for ScFe$_2$ to $1.83\mu_B$ for $\text{Sc}_{0.5}\text{Zr}_{0.5}\text{Fe}_2$ in the range of compositions $0 \leqslant x \leqslant 0.5$ and then, on increase of zirconium content of the alloys, we find that μ(Fe) remains constant to within the limits of the experimental error, and its value is $\mu(\text{Fe}) = 1.83 \pm 0.03\mu_B$ for compositions $0.5 \leqslant x \leqslant 1$.

The magnetic moment substituted into the expressions for μ_f and for the magnetic moments of the iron atoms μ(Fe) used in the relationship $\mu_f = 2\mu(\text{Fe}) + \mu(\text{Sc, Zr})$ yield estimates of the magnetic moments of the states (sites) in the lattice occupied by the atoms of scandium and zirconium μ(Sc, Zr). The values of μ(Sc, Zr) are also listed in Table I. The error in μ(Sc, Zr) is $\pm 0.05\mu_B$ and is mainly due to the scatter of the values of μ_f. Our results thus demonstrate that the atoms of scandium and zirconium in the Laves iron compounds have negative magnetic moments, and we find that $\mu(\text{Sc}) = -1.02 \pm 0.05\mu_B$ for ScFe$_2$ and $\mu(\text{Zr}) = -0.46 \pm 0.05\mu_B$ for ZrFe$_2$. The estimated magnetic moments of the iron μ(Fe) and zirconium μ(Zr) atoms in ZrFe$_2$ agree with those calculated from the electron structure,[15,16] which gives $\mu(\text{Fe}) = 1.87\mu_B$ and $\mu(\text{Zr}) = -0.53\mu_B$. It follows from Table I that in the range of compositions $0.5 \leqslant x \leqslant 1$ the value of μ(Sc, Zr) remains constant within the limits of experimental error and its value is $-(0.46\text{–}0.52)\mu_B$. For compositions in the range $0 \leqslant x \leqslant 0.5$ the magnetic moment of the states occupied by scandium and zirconium atoms decreases in the absolute sense (almost linearly) from $1.02\mu_B$ to $0.52\mu_B$ when scandium is replaced with zirconium.

An increase in x in the investigated system of alloys results in the replacement of a 3d atom of scandium with a 4d atom of zirconium, i.e., the electron system acquires an additional d electron. In the case of the cubic Laves phases it has been shown[17] that an increase in the interatomic distance between the nearest iron atoms (on expansion of the lattice) increases almost linearly the magnetic moment of these atoms. This effect is observed also for $\text{Sc}_{1-x}\text{Zr}_x\text{Fe}_2$ in the range of compositions $0 \leqslant x \leqslant 0.5$. For compositions with $0.5 \leqslant x \leqslant 1$ the lattice period remains constant and so does the magnetic moment of the iron atoms. However, a slight increase in the lattice period in the range $0 \leqslant x \leqslant 0.5$ reduces somewhat (by a factor of almost 2) the magnetic moment of the A = Sc, Zr atoms. According to the electron structure calculations, the increase in the lattice period in the cubic Laves compounds should also increase the magnetic moment of the 4d atom μ(Zr), since the local density of states of the atoms of iron and zirconium is then higher and is concentrated in a narrower interval. We are not aware of any investigations or calculations of the energy structure of cubic Laves AFe$_2$ phases when A is a 3d atom.

It is reported in Refs. 15 and 16 that in the case of cubic AFe$_2$ alloys (A = Zu, Zr, etc.) the hybridization of the 4d (or 5d) states of the A atom with the 3d states of the Fe atom is important in interpretation of the negative magnetic moments of the A atoms. In particular, it is shown there that the 4d states of the A atoms are located at higher energies than the 3d states of the Fe atoms. In the magnetized state of iron the 4d energy bands with the up and down spins shift toward lower and higher energies, respectively. Hybridization of the 3d band of Fe with the 4d band of A with the down spin becomes stronger than for the states with the up spin, i.e., the 4d energy band of zirconium with the down spin merges to a greater extent with the 3d band of iron than does the 4d band of zirconium with the up spin. The integrated number n(A) of the d electrons with the down spin at the A atoms increases compared with n(A) for the up spin. These calculations of the electron structure account for the rise of μ(Fe) when expands the lattice and also for the negative value of μ(A), whereas the difference between the hybridization in the bands with the up and down spins is important for the understanding of the magnetic properties of the cubic Laves compounds.

The experimental results of the present study demonstrate that in the case of $\text{Sc}_{1-x}\text{Zr}_x\text{Fe}_2$ alloys the replacement of scandium with zirconium reduces the hyperfine field $|H(\text{Sc})|$ from 103.4 kOe when $x = 0$ to 63.8 kOe when $x = 1$. The hyperfine field of the ^{91}Zr nuclei $|H(\text{Zr})|$ also decreases when scandium is replaced with zirconium, from 143.7 kOe for $x = 0.8$ to 128.7 kOe for $x = 1$. These changes in the hyperfine fields of H(Sc) and H(Zr) are uncorrelated with the composition dependences of the magnetic moments of the iron atoms μ(Fe) and in the range of compositions $0.5 \leqslant x \leqslant 1$ the value of μ(Fe) remains constant, whereas the hyperfine fields H(Sc) and H(Zr) decrease considerably. There is some correspondence between the composition dependences of the hyperfine fields at the ^{45}Sc and ^{91}Zr nuclei and the magnetic moments of the states occupied by scandium and zirconium atoms μ(Sc, Zr), namely in the range of compositions $0 \leqslant x \leqslant 0.5$ we find that $|H(\text{Sc})|$ and $|\mu(\text{Sc, Zr})|$ decrease on increase in x. These data demonstrate that the change in the magnetic moments of the scandium and zirconium atoms is responsible, more than the change in the magnetic moments of iron, for the composition dependences of H(Sc) and H(Zr) in the $\text{Sc}_{1-x}\text{Zr}_x\text{Fe}_2$ Laves compounds.

It follows from Table I that the atoms of scandium and zirconium have magnetic moments so that the hyperfine fields of the ^{45}Sc and ^{91}Zr nuclei can be described by expressions similar to Eqs. (1), (2), and (3), i.e.,

$$H(\text{Sc}) = H_{\text{loc}}(\text{Sc}) + H_{\text{ind}}(\text{Sc}) = P(\text{Sc})\,\mu(\text{Sc}) + A_s(\text{Sc})\,n_1p_1\mu(\text{Fe})$$
$$+ A_s(\text{Sc})\,n_2p_2\mu(\text{Sc, Zr}) = P(\text{Sc})\,\mu(\text{Sc})$$

$$+A_1(\mathrm{Sc})\mu(\mathrm{Fe})+A_2(\mathrm{Sc})\mu(\mathrm{Sc},\ \mathrm{Zr}), \qquad (5)$$

$$\begin{aligned} H(\mathrm{Zr}) &= H_{\mathrm{loc}}(\mathrm{Zr})+H_{\mathrm{ind}}(\mathrm{Zr})=P(\mathrm{Zr})\mu(\mathrm{Zr}) \\ &\quad +A_s(\mathrm{Zr})n_1'p_1'\mu(\mathrm{Fe}) \\ &\quad +A_s(\mathrm{Zr})n_2'p_2'\mu(\mathrm{Sc},\ \mathrm{Zr}) \qquad (6) \\ &= P(\mathrm{Zr})\mu(\mathrm{Zr})+B_1(\mathrm{Zr})\mu(\mathrm{Fe})+B_2(\mathrm{Zr})\mu(\mathrm{Sc},\ \mathrm{Zr}), \end{aligned}$$

where $P(\mathrm{Sc})$ and $P(\mathrm{Zr})$ are the polarization constants for the magnetic moments of the scandium and zirconium atoms, whereas A_1, A_2, B_1, and B_2 are the constants of proportionality equal to the products of n, p, and A_s for the respective contributions of the first and second coordination spheres to the states of scandium and zirconium, where $P(\mathrm{Sc})\mu(\mathrm{Sc})$ or $P(\mathrm{Zr})\mu(\mathrm{Zr})$ represent the contributions made to the hyperfine fields of ^{45}Sc or ^{91}Zr by the magnetic moments of the scandium and zirconium atoms, $A_1(\mathrm{Sc})\mu(\mathrm{Fe}) = A_s(\mathrm{Sc})n_1p_1\mu(\mathrm{Fe})$ or $B_1\mu(\mathrm{Fe}) = A_s(\mathrm{Zr})n_1'p_1'\mu(\mathrm{Fe})$ are the contributions to the hyperfine fields of ^{45}Sc and ^{91}Zr made by the magnetic moments of the iron atoms in the first coordination sphere, and $A_2(\mathrm{Sc})n_2'p_2'\mu(\mathrm{Sc, Zr})$ and $B_2 = A_s(\mathrm{Zr})n_2'p_2'\mu(\mathrm{Sc, Zr})$ are the contributions to the hyperfine fields of ^{45}Sc and ^{91}Zr made by the magnetic moments of the scandium and zirconium atoms in the second coordination sphere. The physical sources of these contributions were discussed earlier in connection with Eqs. (1), (2), and (3). Equations (5) and (6) can be used, for a given composition, to identify the separate NMR peaks of ^{45}Sc and ^{91}Zr. Let us consider the $\mathrm{ZrFe_2}$ alloys containing scandium impurities. In the case of $\mathrm{Sc_{0.02}Zr_{0.98}Fe_2}$ the difference ΔH between the hyperfine fields of ^{91}Zr corresponding to the main and the first allowed lines in the NMR spectrum of ^{91}Zr amounts to $\Delta H(\mathrm{Zr}) = +5.54$ kOe. The corresponding difference between the hyperfine fields of ^{45}Sc in the NMR spectrum of ^{45}Sc in the same alloy is $\Delta H(\mathrm{Sc}) = +2.42$ kOe. Bearing in mind that $\mu(\mathrm{Fe})$ does not change in this range of compositions, it follows from Eqs. (5) and (6) that $\Delta H(\mathrm{Zr}) = A_s(\mathrm{Zr})n_2'p_2'\Delta\mu(\mathrm{Sc, Zr})$ and $\Delta H(\mathrm{Sc}) = A_s(\mathrm{Sc})n_2'p_2'\Delta\mu(\mathrm{Sc, Zr})$. Since $n_2'p_2' = n_1'p_1'$ for a given alloy, the ratio of the theoretical shifts of the hyperfine fields for the ^{91}Zr and ^{45}Sc nuclei is

$$\Delta H(\mathrm{Zr})/\Delta H(\mathrm{Sc})=A_s(\mathrm{Zr})/A_s(\mathrm{Sc})=2.30$$

[$A_s(\mathrm{Zr}) = 2000$ kOe per one s electron and $A_s(\mathrm{Sc}) = 780$ kOe per one s electron]. This ratio agrees with the experimental value $\Delta H(\mathrm{Zr})_{\mathrm{exp}}/\Delta H(\mathrm{Sc})_{\mathrm{exp}} = 2.29$. The results just quoted provide additional evidence that the NMR peaks of ^{45}Sc and ^{91}Zr in $\mathrm{Sc_{1-x}Zr_xFe_2}$ with $0.9 \leqslant x \leqslant 1$ are due to the shifts of the hyperfine fields of ^{91}Zr and ^{45}Sc resulting from the replacement of zirconium with scandium in the second coordination sphere, from the corresponding change in the average magnetic moment of the second coordination sphere, and from the different values of $\mu(\mathrm{Zr})$ and $\mu(\mathrm{Sc})$ in the alloys.

The shift of the hyperfine field $H(\mathrm{Sc})$ in the case of $\mathrm{ScFe_2}$ observed on replacement of scandium with zirconium is $\Delta H(\mathrm{Sc}) = -1.16$ kOe, which is approximately half the shift of $\Delta H(\mathrm{Sc})$ in $\mathrm{ZrFe_2}$ when zirconium is replaced with scandium. Since the addition of zirconium to $\mathrm{ScFe_2}$ alters the magnetic moments of scandium $\mu(\mathrm{Sc})$ and iron $\mu(\mathrm{Fe})$ in the first coordination sphere, and of scandium and zirconium $\mu(\mathrm{Sc, Zr})$ in the second coordination sphere of scandium, it follows from Eq. (5) that the shifts of the hyperfine fields $H(\mathrm{Sc})$ and broadening of the NMR spectra of ^{45}Sc may occur because of changes in $H(\mathrm{Sc})$ due to all the terms in Eq. (5). A correct estimate of the magnetic moments $\mu(\mathrm{Sc})$ and $\mu(\mathrm{Zr})$ and estimates of the various contributions to the hyperfine fields $H(\mathrm{Sc})$ and $H(\mathrm{Zr})$ can be made only if we know the constants $P(\mathrm{Sc})$ and $P(\mathrm{Zr})$ as well as the coefficients A_1, A_2, B_1, and B_2 in Eqs. (5) and (6). However, there is no published information on these constants and coefficients. Moreover, there are at present no data on the hyperfine fields of the impurity nuclei of nonmagnetic atoms occupying the scandium and zirconium sites in $\mathrm{Sc_{1-x}Zr_xFe_2}$, so that we cannot apply the scaling method in order to estimate $H_{\mathrm{ind}}(\mathrm{Sc})$ and $H_{\mathrm{ind}}(\mathrm{Zr})$. Further experiments are needed in order to be able to estimate $\mu(\mathrm{Sc})$ and $\mu(\mathrm{Zr})$ and also the main contributions to the hyperfine fields $H(\mathrm{Sc})$ and $H(\mathrm{Zr})$.

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Translated by A. Tybulewicz