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Abstract. A combined nuclear magnetic resonance (NMR) and Mössbauer effect study of $YFe_{10}V_2$ has been carried out. Based on the ^{57}Fe hyperfine fields (HFS) obtained from the Mössbauer results, the resonance lines of the NMR spectrum are assigned and the site preference of V atoms is determined. On the other hand, according to the site preference of vanadium atoms determined by NMR, together with neutron diffraction results, the ^{57}Fe Mössbauer spectrum is fitted. It can be deduced from the NMR results that the existence of one nearest-neighbour Fe atom leads to an increase in the V HF of about 0.35, and the core electron polarization contribution H_{cp}, the 4s conduction electron polarization contribution H_s and the effect of the second-nearest-neighbour Fe atoms on the HF sites cannot be negligible.

1. Introduction

Recently, a great deal of interest has focused on the ternary compounds $RFe_{12-x}T_x$ (R ≡ rare earth elements and T ≡ Ti, V, Cr, Mo, W or Si) with the $ThMn_{12}$ structure for their potential application as permanent magnets. Although RFe_{12} does not exist for any rare earth, $RFe_{12-x}T_x$ compounds with the $ThMn_{12}$ structure can be stabilized by T ≡ Ti or W when $x = 1$ or by T ≡ V, Cr, Mo or Si when $x = 2$ [1–4]. In 1990, Yang and co-workers discovered that rare-earth–iron intermetallic compounds of the type $RFe_{11}Ti$ can absorb moderate quantities of nitrogen at 500 °C, giving the approximate composition $RFe_{11}TiN_{0.5}$ at 1 atm. Its structure is retained, but its Curie temperature is enhanced by about 200 K and the iron moment increases by about 17%. More significantly, the anisotropy of $NdFe_{11}TiN_{0.5}$ has an easy axis with an anisotropy field of about 8 T at room temperature. Therefore, $NdFe_{11}TiN_x$ can become a novel permanent magnet [5]. In the $RFe_{12-x}T_x$ phase, R atoms occupy the single 2a site, and T atoms share the three different sites 8i, 8j and 8f with Fe atoms with some site preference [6–9]. This makes the hyperfine field (HF) distribution for $RFe_{12-x}T_x$ very complex. In order to measure the HF distribution for these samples more directly and more precisely, a combined nuclear magnetic resonance (NMR) and Mössbauer effect (ME) study is undetaken. Both NMR and the ME technique are important methods for researching the hyperfine interaction, but each technique has some advantages and weaknesses. NMR can measure the HF value more directly and more precisely while, in ME experiments, some difficulty may exist in decomposing the superimposed ME sextets; however, much care is needed in NMR experiments to obtain actual intensities while intensities are more directly obtained in ME measurements. In this paper, the magnetism

and HFS of $YFe_{10}V_2$ are investigated by the means of zero-field spin-echo NMR and ME techniques. On the basis of the results obtained here, we discuss the site preference of vanadium atoms and the correlation of the ^{51}V HF with the V local atomic environment in this sample.

2. Experimental details

The button samples were prepared by arc melting under a highly pure argon atmosphere. The purities of the raw materials were better than 99.5% for Y and 99.9% for Fe and V. As-cast ingots were wrapped in Permalloy foil and annealed in a vacuum quartz tube at 850 °C for 2 weeks.

X-ray diffraction patterns obtained from powder samples identified that the main phase of the annealed samples is a tetragonal phase with a $ThMn_{12}$ structure. The magnetization was measured using a magnetometer with a superconducting coil providing an external field up to 7 T at 1.5 K. The value of the spontaneous magnetization $\sigma_s(0)$ was derived from the high-field portion of the σ^2 versus H/σ curve by extrapolation to zero field.

Zero-field spin-echo NMR measurements of the HF distribution were made at a temperature of 8 K for frequencies ranging from 30.0 to 70.0 MHz. In order to obtain this low temperature without the consumption of liquid helium, the powder samples were mixed with a thermal compound and then glued to the cold end of a closed-cycle refrigerator. The pulse sequence 1.5–60–1.5 μs at constant amplitude corresponding to the maximum intensity was applied. The spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2 for different peaks were determined by the spin-echo intensity versus the pulse recovery time and the distance between two pulses, respectively. The spin-echo amplitude was measured by a delay square signal with the same frequency as the spin-echo signal; both of them were recorded and accumulated many times using a computer. The Mössbauer spectrum (MS) was obtained at liquid-nitrogen temperature using a constant-acceleration spectrometer with a $^{57}Co(Pd)$ source. The isomer shift (IS) is relative to α-Fe at room temperature.

3. Results and discussion

3.1. NMR and Mössbauer results

Figure 1 shows the spin-echo NMR spectrum of $YFe_{10}V_2$ obtained at a temperature of 8 K. This spectrum consists of six resolved peaks at 63.5, 57.5, 53.5, 49.0, 45.0 and 42.0 MHz. Since the spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2 for various peaks differ from one another, a correction for T_1 and T_2 was used in plotting figure 1.

The ^{57}Fe MS of $YFe_{10}V_2$ measured at 77 K is presented in figure 2. It is obvious that a fit with only three Lorentzian sextets taking into account the different contributions of the iron atoms located at the three non-equivalent crystallographic sites 8i, 8j and 8f cannot satisfactorily describe the complexity of the spectrum. Its complexity is due to the distribution of the two 3d transition metals (iron and vanadium) over the three types of crystallographic site occurring in the $ThMn_{12}$ structure. In this respect a preferential occupation of the sites by vanadium or iron plays an important role and can be used as a clue to understanding the ^{57}Fe MS. Thus, it is necessary to make a combined NMR and Mössbauer study to determine the HF and the site preference of V atoms.
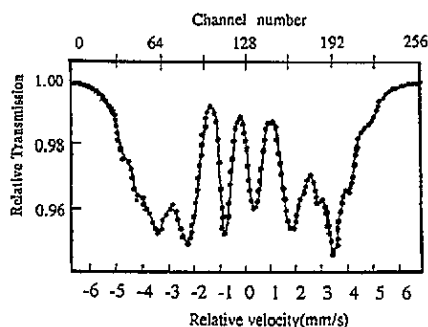
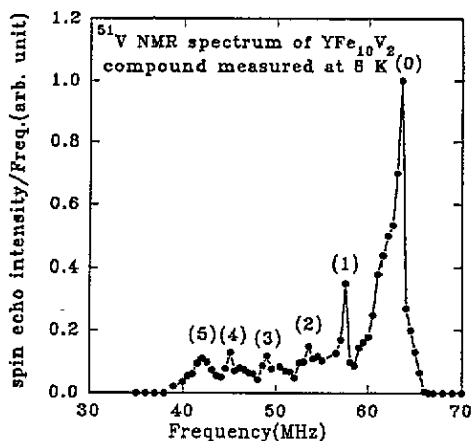**Figure 1.** Spin-echo NMR spectrum of YFe$_{10}$V$_2$ obtained at 8 K.

Figure 2. MS of YFe$_{10}$V$_2$ measured at liquid nitrogen temperature.

3.2. Assignment of the NMR spectrum and the site preference of V atoms

In the YFe$_{10}$V$_2$ sample, the ^{89}Y, ^{57}Fe and ^{51}V are good resonant nuclei and their resonant frequencies are distributed from 20 to 80 MHz. This may make the resonant lines very complicated. Thus, first of all, it is necessary to assign the NMR spectra. Although the relative NMR sensitivity of the ^{57}Fe nucleus is comparable with those of ^{89}Y and ^{51}V, the natural abundance of the former is almost two orders of magnitude smaller than those of the latter, so that the integral intensity of the ^{57}Fe signals is more than one order of magnitude lowr than those of ^{89}Y and ^{51}V. On the other hand, it can be seen from figure 2 that the largest ^{57}Fe HF is less than 28 T. Because the measured temperature for NMR is different from that for the MF, a direct comparison between HF values derived from NMR and the MS is difficult, but the MS indicates that the region of the Fe NMR frequency of this phase ends at about 40 MHz (30 T). For this reason the NMR signals between 40 and 70 MHz are not due to the ^{57}Fe nuclei, but to ^{51}V and ^{89}Y.

Although the isotopic abundance for ^{89}Y (100%) is almost equal to that of ^{51}V (99.76%), the nuclear magnetic moment of the former is smaller than that of the latter, and, as a consequence, the integral intensity of the ^{89}Y NMR signal is much weaker than that of ^{51}V. Thus, the main resonance lines of this sample arise from the ^{51}V. Support for this assignment is the comparison of the HF values at the Y and V sites with those at the Fe sites. Here, we take the most intense peaks centred at 63.5 MHz as an example; if this signal is assigned as originating from ^{89}Y in the 2a site of YFe$_{10}$V$_2$, according to the formula

$$f = \gamma \times H \tag{1}$$

where the gyromagnetic ratio γ is 2.1 MHz T^{-1} for ^{89}Y, then the HF value at Y sites corresponding to this peak is 30.5 T, which is larger than that of Fe sites. Since Y atoms have a non-magnetic moment, the HF at its nucleus arises only from the 4s spin polarization due to neighbouring Fe moments, so that it must be smaller than that of Fe sites. Therefore, the signals are not attributed to ^{89}Y. However, if this line comes from ^{51}V, its HF value is only 5.67 T. Based on the HF value, the peaks located at 42.0 MHz could originate from ^{89}Y nuclei, e.g. the ^{89}Y NMR peak of Y$_2$Fe$_{17}$ is located at 42.0 MHz [10] but, as discussed

above, the intensity of the ^{51}V signal is much stronger than that of ^{89}Y. So, it is reasonable to assign the lines to ^{51}V.

The ^{51}V NMR spectrum of this sample consists of a series of six almost equally spaced peaks. It is very similar to that of $Fe_{3-x}V_xSi$ alloys [11]. Table 1 lists the nearest-neighbour (NN) environments of the sites in the $ThMn_{12}$ structure [12]. From table 1, we can see that 8f (or 8j) sites have only two NN 8f (or 8j) sites, and the 8i sites have five NN 8i sites. If the V atoms enter 8f or 8j sites, the spectra should show a series of three peaks. If the vanadium atoms enter both 8j and 8f sites, at least 15 NN sites may exist; this will make the NMR spectrum too complicated to resolve. So we can conclude that the V atoms prefer to occupy the 8i sites, which is in agreement with neutron diffraction results [6–9]. This provides a good opportunity of investigating the site preference utilizing NMR. Studies of the selective site substitutions of transition-metal impurities in the Fe_3Si matrix by the NMR technique have been made in previous investigations [11, 13, 14]. Because the V atoms occupy 8i sites only randomly and the 8i site has five NN Fe(V) atoms in 8i sites, the lines centred around 63.5, 57.5, 53.5, 49.0, 45.0 and 42.0 MHz arise from ^{51}V with zero, one, two, three, four and five NN V atoms, respectively. These assignments are labelled in figure 1 and listed in table 2. The unresolved shoulder on the left-hand side of the strongest peak may be caused by asymmetry of the electric field gradient. Unresolved satellites also occur around other peaks.

Table 1. Site nearest-neighbour environments in the $ThMn_{12}$ structure [12].

Site	Number of the following sites as NNS			
	2a	8i	8j	8f
2a	—	4	8	8
8i	1	5	4	4
8j	2	4	2	4
8f	2	4	4	2

Table 2. Frequencies corresponding to the centres of gravity of ^{51}V NMR lines, corresponding to the hyperfine parameter B; C is the transferred hyperfine coupling constant.

n_{Fe}	n_V	f (MHz)	B (T)	C (T/μ_B)
13	0	63.5	5.67	
12	1	57.5	5.13	
11	2	53.5	4.78	
10	3	49.0	4.38	0.23
9	4	45.0	4.02	
8	5	42.0	3.75	

Recently, the MSs of $RFe_{12-x}V_x$ were analysed satisfactorily by considering the preferential occupation of the vanadium atoms and using a binomial distribution to calculate the probability of the possible NN configuration [15]. In our work, the MS of $YFe_{10}V_2$ was fitted by this method. Owing to the limit of our fitting program in our laboratory, eight subspectra were employed to fit the spectrum and relative intensities lower than 5% were not considered. From the values of the HFs of the different environments the average HF

Table 3. Hyperfine parameters (77 K), Fe magnetic moment (1.5 K) and saturation magnetization (1.5 K) of YFe$_{10}$V$_2$ alloy. A bar indicates an average value.

$\sigma(0)$(emu g^{-1})	$\bar{\mu}_{Fe}(\mu_B)$	$\bar{H}_{HF}$ (8i)	$\bar{H}_{HF}$ (8j)	$\bar{H}_{HF}$ (8f)	$\bar{I}S$ (mm s^{-1})	$\bar{H}_{HF}$	A(T/μ_B)
113.3	1.52	27.36	20.25	22.92	−0.03	22.82	15.00

of the iron atoms in the three iron sublattice, and the average HF and IS of the whole iron lattice, were derived. These values are listed in table 3.

It is commonly assumed that the relationship between the average HF $\bar{H}_{HF}$ and the average magnetic moment ($\bar{\mu}_{Fe}$) of iron atom can be approximately described by the formula $\bar{H}_{HF} = A\bar{\mu}_{Fe}$, where A is the hyperfine coupling constant. Considering the two non-magnetic elements Y and V, μ_{Fe} can be derived from $\sigma_s(0)$. Comparing $\sigma_s(0)$ with $\bar{H}_{HF}$, we could approximately determine that A is 15.00 T/μ_B for YFe$_{10}$V$_2$. This is also listed in table 3.

As it is different from the ME absorption, the NMR signal comes from a rather complicated mechanism for ferromagnetic substances in that a nucleus couples with the 3d electron moment and, as a consequence, the resonant precession of the nuclear moment also affects the 3d electrons. Since the spin magnetic moment of an electron is much larger than that of a nucleus, the observed signal originates mainly from the motion of the 3d electron moment. Thus the observed NMR signal intensity for a given V site depends not only on the number of V atoms at this site but also on the strength of the nucleus–electron coupling and the mobility of the electronic magnetic moment; the latter is somewhat local atomic environment dependent. Thus the induced spin-echo intensity for a given site may not follow exactly the atomic occupancy.

3.3. Effect of nearest-Fe-neighbour atoms on V hyperfine fields

In the case of 3d transition-metal compounds or alloys, the HF H_{HF} at a 3d magnetic nucleus is assumed to arise from three contributions [16]:

$$H_{HF}(i) = H_{cp}(i) + H_s(i) + H_{sp}(i) \tag{2}$$

where H_{cp} and H_s are due to core electron polarization and 4s conduction electron polarization, respectively; both are proportional to the on-site magnetic moment. H_{sp} is herein called the transferred hyperfine field (THF) caused by neighbouring magnetic atoms and is proportional to the number of NN magnetic atoms and their magnetic moment. Thus,

$$H_{cp}(i) + H_s(i) = A\mu(i) \tag{3}$$

$$H_{sp}(i) = \sum_j C(i)n_j(i)\mu(j) \tag{4}$$

$$H_{HF}(i) = A\mu(i) + \sum_j C(i)n_j(i)\mu(j) \tag{5}$$

where $\mu(i)$ is the on-site magnetic moment of the ith atom, and $\mu(j)$ is the moment of the neighbouring j-site magnetic atom. A and C are the hyperfine coupling constants, and $n_j(i)$ is the number of the j-site magnetic atoms surrounding the ith atom.

Since V atoms have a negligible moment, $H_{cp} + H_s \simeq 0$, and the predominant contribution to the hyperfine fields at V nuclei is the THF. It can be written as [16]

$$H_{HF}(V) = H_{THF}(V) = \sum_j C(i)n_j(i)\mu_{Fe}(j). \tag{6}$$

In equation (6), we approximately use the average Fe moment $\bar{\mu}_{Fe}$ to replace $\mu(j)$ and the average constant C to substitute for $C(i)$. Thus,

$$H_{HF}(V) = Cn(i)\bar{\mu}_{Fe}. \tag{7}$$

Figure 3 indicates the HFs at V sites obtained by NMR experiments at 8 K as a function of the number x of the NN Fe atoms of V sites. From figure 3 and equation (7), it can be deduced that the addition of one NN Fe atom leads to an increase in the ^{51}V HF with a rate of about 0.35 T/Fe atom. From the magnetization measurement, it can be seen that the average iron moment is 1.52 μ_B. According to equation (7) and figure 3, we can calculate that the hyperfine coupling constant C is about 0.23 T/μ_B. Extrapolation of this curve to $n = 0$ yields a very large field contribution (about 0.8 T). This contribution can be attributed not only to a non-vanishing $H_{cp}(V) + H_s(V)$, connected with a very small magnetic moment, but also to the second-nearest-neighbour Fe atoms.
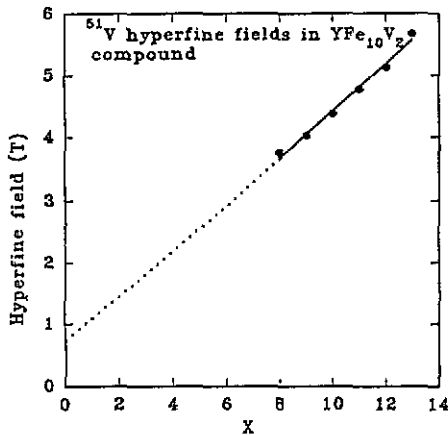

Figure 3. HFS at V sites obtained by NMR experiments as a function of the number x of the NN Fe atoms of V sites.

4. Summary

(1) Comparing the results of NMR with those of ME, we can conclude that the NMR signals between 40 and 70 MHz do not originate from ^{57}Fe and ^{89}Y nuclei, but from ^{51}V nuclei. A combined NMR and ME investigation of $RFe_{12-x}T_x$ can determine the HF in these complicated systems more reliably.

(2) The NMR measurements of the nuclei of vanadium indicate that the vanadium atoms preferentially occupy the 8i site, which is in agreement with neutron diffraction results. This provides an evidence for selective site substitution using the NMR technique.

(3) The HFs at V sites depend linearly on the number of NN Fe atoms, and the core electron polarization contribution H_{pc}, the 4s conduction electron polarization contribution H_s and the effect of second-nearest-neighbour Fe atoms on the HF at V sites cannot be negligible.

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