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Giant moment of $Fe_{16}N_2$ as evidenced by ^{57}Fe NMR studies

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A nuclear-magnetic-resonance study of $Fe_{16}N_2$, Fe_4N, and bcc α-Fe phases, along with magnetization experiments on samples containing these phases, show that the average Fe moment for $Fe_{16}N_2$ is between $2.7\mu_B$ and $2.9\mu_B$. This is in contrast to previous studies which report values ranging from $2.3\mu_B$ to $3.5\mu_B$. The results reported here indicate an average Fe moment for $Fe_{16}N_2$ which is significantly enhanced compared with that for α-Fe, and a moment for Fe atoms at the $4d$ sites which is greater than $3.0\mu_B$. [S0163-1829(96)01225-8]

Although the α''-$Fe_{16}N_2$ phase was discovered more than 40 years ago,[1] its magnetic properties have attracted considerable attention only recently.[2–11] The issue is whether or not this phase has an average Fe moment 30% greater than that for bcc α-Fe, i.e., a so-called ''giant moment.'' If such a giant Fe moment exists, such as that first reported in 1971,[12] then the fact that an Fe atom can carry a moment of about $3\mu_B$ in Fe metallics should stimulate a major effort to explore additional metallic materials with high saturation magnetization. Also, this will have an impact on the theory of magnetism of $3d$ metals since such a large moment is unexpected from band theory. However, after four decades of study on this phase, pure single-phase $Fe_{16}N_2$ has not yet been produced in bulk form due to fundamental difficulties.[1,6] All of the samples studied to date contained a large amount of bcc α-Fe and γ-Fe(N) (a nonferromagnetic fcc phase). The saturation magnetization for $Fe_{16}N_2$ has to be obtained by subtracting the contributions of these phases from the total saturation magnetization, which involves the difficult task of determining the phase composition quantitatively. The average Fe moment of the $Fe_{16}N_2$ phase reported by different groups varies over a wide range from $2.3\mu_B$ to $3.5\mu_B$ (see the review by Metzger, Bao, and Carbucicchio[9]). If one relies solely on the magnetization measurements, then the controversy regarding the Fe moment of $Fe_{16}N_2$ will remain until a single-phase sample is prepared, which is unlikely to be realized anytime soon. In order to resolve the controversy, it is essential to utilize an approach which provides information concerning the Fe moments for each individual phase (or Fe site) without requiring a knowledge of the phase composition. Hyperfine interaction experiments offer such an alternate means as the Fe hyperfine field (HF) for a given site provides a measure of the Fe moment. Within the Fe-N family, there are some similarities in the structure and magnetic properties between the Fe_4N and $Fe_{16}N_2$ phases. Therefore, the relationship between hyperfine fields and atomic moments for Fe_4N provides important insight in the understanding of the local magnetic properties of $Fe_{16}N_2$. In this paper, we present an observation of nuclear magnetic resonance (NMR) in the $Fe_{16}N_2$ phase, and a comparative HF study of $Fe_{16}N_2$, Fe_4N, and α-Fe, focusing on the question of a giant Fe magnetic moment in the $Fe_{16}N_2$ phase.

The Fe_4N single phase and $Fe_{16}N_2$ samples used in this study were prepared following essentially the method originated by Lehrer[13] and Jack[1] several decades ago. We refer the reader to Refs. 4–6 for the details of the sample preparation. The phase constituents of the samples were identified using x-ray diffraction (XRD) and NMR. We note that NMR is a much more sensitive technique than XRD for detecting a trace amount of α-Fe, which is characterized by a sharp ^{57}Fe resonance peak at 46.7 MHz. The $Fe_{16}N_2$ sample consisted of three phases: α''-$Fe_{16}N_2$, α-Fe, and γ-Fe(N). The α''-$Fe_{16}N_2$ content was about 50 wt. %. A careful search for α-Fe in the Fe_4N sample was carried out at 1.3 K by NMR with various experimental conditions, and none was observed.

The magnetization curves for the two samples were obtained at 4.5 K using a superconducting quantum interference device magnetometer. The results are shown in Fig. 1. Also shown in Fig. 1 is the magnetization curve for α-Fe as a reference. The saturation magnetization values for these

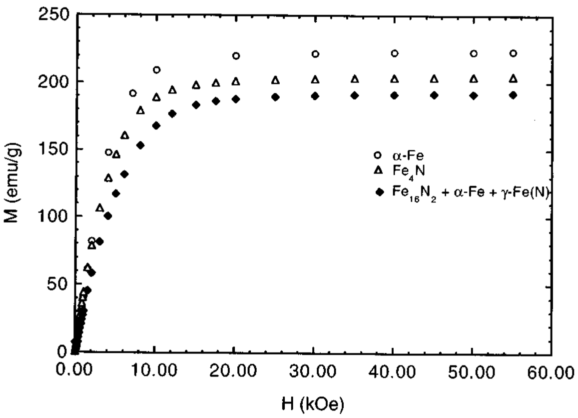

FIG. 1. Magnetization M in emu/g vs magnetic field H in kOe measured at 4.5 K: open circles, bcc α-Fe; open triangles, Fe_4N; closed diamonds, $Fe_{16}N_2$.

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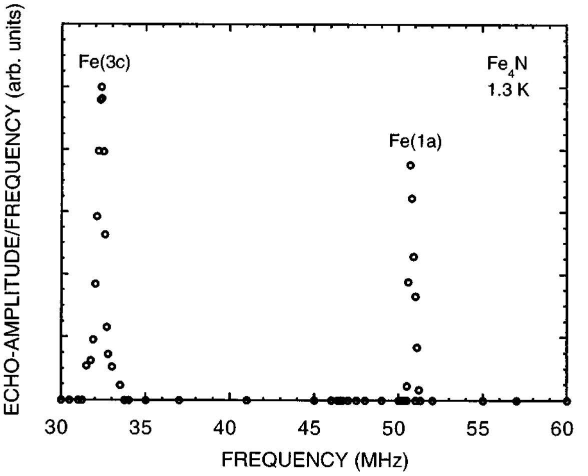

FIG. 2. ^{57}Fe spin-echo NMR spectrum obtained from the Fe_4N sample at 1.3 K.

samples are 226 emu/g (or an Fe moment of $2.26\mu_B$) for the α-Fe phase, 205 emu/g (or an average Fe moment $\overline{\mu_{\rm Fe}}=2.18\mu_B$) for the Fe_4N phase, and 196 emu/g for the $Fe_{16}N_2$ sample from which the saturation magnetization for the $Fe_{16}N_2$ phase was deduced to be 280 emu/g ($\overline{\mu_{\rm Fe}}=2.9\mu_B$).[6]

The ^{57}Fe hyperfine field measurements were carried out at 1.3 K using a coherent spin-echo NMR spectrometer for frequencies ranging from 10 to 300 MHz. Figure 2 shows the NMR spectrum obtained from the Fe_4N sample. Two ^{57}Fe peaks were observed at 32.3 and 50.7 MHz with a relative intensity (area) ratio of about 3:1, respectively. These correspond to ^{57}Fe HF's of 235 and 369 kOe, respectively. Based on the intensities, the 32.3- and 50.7-MHz peaks are assigned to the face center [Fe($3c$)] and the corner [Fe($1a$)] Fe sites, respectively, consistent with the previous assignment for this compound.[14] Figure 3 shows the ^{57}Fe spectrum obtained from the $Fe_{16}N_2$ sample. In addition to the 46.7-MHz α-Fe peak, there are three peaks centered at 42.1, 45.2, and 57.3 MHz, which correspond to ^{57}Fe HF's of 307, 329, and 418 kOe, respectively. The relative intensities (areas) for the 42.1- and 57.3-MHz peaks are about the same, and are about half of that for the 45.2-MHz peak. The ^{57}Fe NMR frequency in Fe_3N is 35.6 MHz.[14] Therefore, it is concluded that the $Fe_{16}N_2$ sample studied contains no Fe_3N or Fe_4N phases. Based on the relative intensities (areas) and the corresponding HF values, the 42.1-, 45.2-, and 57.3-MHz peaks are assigned to the Fe($4e$), Fe($8h$), and Fe($4d$) sites, respectively. The HF values obtained from the present NMR experiments are close to most Mössbauer effect (ME) experimental results,[10,15,16] with one exception in that the HF value for the Fe($4d$) site obtained by NMR is slightly greater than that obtained from ME. The very sharp NMR spectra shown in Figs. 2 and 3 indicates the small orbital and dipolar fields in these two systems.

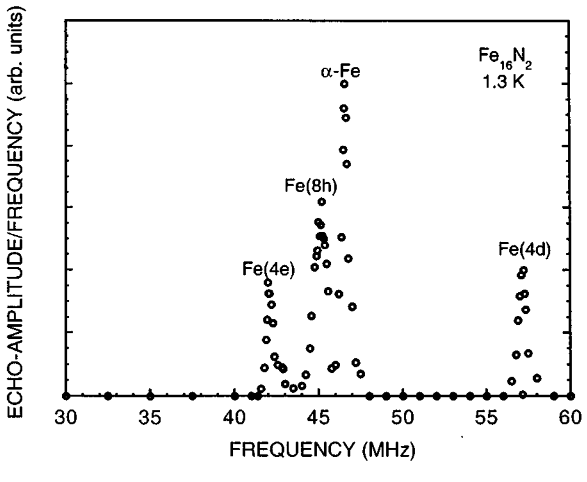

FIG. 3. ^{57}Fe spin-echo NMR spectrum obtained from the $Fe_{16}N_2$ sample at 1.3 K.

The total HF, $H_{\rm hf}$, produced by s electron polarization at a given $3d$ atom, in this case Fe, is often thought of as arising from three contributions,[17] and can be written

$$H_{\rm hf}(i)=H_{\rm cp}(i)+H_s(i)+H_{\rm sp}(i). \tag{1}$$

In Eq. (1), $H_{\rm cp}$ and H_s denote the contributions from the spin polarizations of the inner-core s electrons and the outer $4s$ electrons, respectively, by the $3d$ electrons of the Fe atom itself and, consequently, are approximately proportional to the on-site moment $\mu_{\rm Fe}(i)$. $H_{\rm sp}$ denotes the contribution from the $4s$ electron polarization due to the nearest-neighbor Fe atoms, and is approximately proportional to the number of the nearest Fe neighbors, $n(i)$, and their average atomic moments $\overline{\mu_{\rm Fe}}$. Hence,

$$H_{\rm cp}(i)+H_s(i)=a\mu_{\rm Fe}(i) \quad \text{and} \quad H_{\rm sp}(i)=cn(i)\overline{\mu_{\rm Fe}}, \tag{2}$$

where a and c are the hyperfine coupling constants. The fact that $H_{\rm cp}+H_s$ is dominant for Fe-based systems, and that the average moment of Fe atoms in the nearest neighbor shell is not significantly different from that of the on-site moment, lead to the following approximate expression which is generally used within a specific system:

$$H_{\rm hf}(i)\simeq A\mu_{\rm Fe}(i), \tag{3}$$

where A is the effective hyperfine coupling constant due to spin polarization. For a given Fe atom, A is dependent on its electronic state and the configuration of the neighboring Fe atoms, including the symmetry of the distribution of these Fe atoms and distances of the Fe atom to these neighboring Fe atoms. For Fe ionic compounds, there are no conduction electrons and, hence, $H_s=0$ and $H_{\rm sp}\simeq 0$. The experiments on ferrites have shown that the contribution of core polarization to the Fe HF leads to $a\simeq 110$ kOe/μ_B.[18] For Fe metallic systems, $H_{\rm sp}$ has a significant contribution to the total HF, leading to $A>a$. α-Fe, for which $H_{\rm hf}=340$ kOe (Fig. 3) and $\mu_{\rm Fe}=2.26\mu_B$ (Fig. 1), is a typical example of such Fe metallics, and has $A=150$ kOe/μ_B. For a majority of the Fe-based materials, A varies over a range of values from approximately 110 to 150 kOe/μ_B (from ionic to metallic).

Fe_4N has the fcc structure. The number of the nearest Fe neighbors for the $1a$ and $3c$ Fe sites in Fe_4N is the same (12). The difference between these two sites is that there are two N atoms in the nearest-neighbor shell surrounding the $3c$ site, while no N atoms surround the $1a$ site. The Fe moments at the $1a$ and $3c$ sites have been determined by neutron diffraction (ND) to be $2.98\mu_B$ and $2.01\mu_B$, respectively.[19] Substituting these values into Eq. (3), the hyperfine coupling constant values are found to be 124 and 117 kOe/μ_B for the Fe($1a$) and Fe($3c$), respectively. Combining the total Fe moments obtained from magnetization measurements (Fig. 1), and taking the NMR frequencies (Fig. 2) as relative measures of the Fe moments at the $1a$ and $3c$ sites, we have

$$\mu_{\mathrm{Fe}}(1a)+3\mu_{\mathrm{Fe}}(3c)=8.71\mu_B$$

and

$$\mu_{\mathrm{Fe}}(1a)=1.57\mu_{\mathrm{Fe}}(3c). \qquad (4)$$

Thus it is found that $\mu_{\mathrm{Fe}}(1a)=2.99\mu_B$, $\mu_{\mathrm{Fe}}(3c)=1.91\mu_B$, and $A(\mathrm{Fe_4N})=123$ kOe/μ_B. The excellent agreement between the NMR and ND results for $\mathrm{Fe_4N}$ indicates that HF experiments might be an effective means of obtaining information concerning the Fe atomic moment in Fe-N systems. Also, these results indicate that the N-Fe interaction results in a decrease in the Fe moment and, consequently, the Fe HF, whereas it does not affect the hyperfine coupling constant.

$\mathrm{Fe_{16}N_2}$ has a definite structural relationship with α-Fe and $\mathrm{Fe_4N}$. If one takes the number of Fe atoms within 2.866 Å (the lattice parameter of bcc α-Fe) as the number of Fe nearest neighbors, then the $\mathrm{Fe_{16}N_2}$ lattice can be regarded as a distorted $\mathrm{Fe_4N}$ structure. The $4d$, $8h$, and $4e$ sites have 12, 12, and 13 Fe atoms, respectively, with the same average distance of 2.65 Å. Based on the similarity between the two phases, it is expected that $A(\mathrm{Fe_{16}N_2})$ and $A(\mathrm{Fe_4N})$ are close to each other. Furthermore, the local atomic environments for Fe sites in $\mathrm{Fe_{16}N_2}$ are similar to that in $\mathrm{Fe_4N}$, for which each Fe has 12 Fe atoms as the nearest neighbors at 2.68 Å. In particular, the $4d$ site for $\mathrm{Fe_{16}N_2}$ is similar to the $1a$ site for $\mathrm{Fe_4N}$ in that both sites have no N as nearest neighbors. The $8h$ and $4e$ sites for $\mathrm{Fe_{16}N_2}$ are similar to the $3c$ site for $\mathrm{Fe_4N}$, with the principal difference being that the $8h$ and $4e$ sites in $\mathrm{Fe_{16}N_2}$ have one N nearest neighbor, while the $3c$ site in $\mathrm{Fe_4N}$ has two N nearest neighbors. From these considerations, one expects that $\mu_{\mathrm{Fe}}(4d)$ is much greater than $\mu_{\mathrm{Fe}}(8h)$ and $\mu_{\mathrm{Fe}}(4e)$, and that $\mu_{\mathrm{Fe}}(8h)$ and $\mu_{\mathrm{Fe}}(4e)$ are nearly equal to each other with $\mu_{\mathrm{Fe}}(8h)$ being slightly greater. As shown in Fig. 3, the high ^{57}Fe HF value for the $4d$ site and the much lower and very close HF values for the $4e$ and $8h$ sites are consistent with the above-mentioned picture. Therefore, it is expected that the effective hyperfine coupling constant values for the three Fe sites are, just as found in $\mathrm{Fe_4N}$, nearly equal to each other. Hence, the ^{57}Fe HF value for a given Fe site can be taken as a measure of the relative magnitude of the Fe moment at that site, namely,

$$\mu_{\mathrm{Fe}}(4e):\mu_{\mathrm{Fe}}(8h):\mu_{\mathrm{Fe}}(4d)=1.00:1.07:1.36. \qquad (5)$$

The value of the *average* Fe moment for $\mathrm{Fe_{16}N_2}$ reported by the researchers in favor of a giant Fe moment ranges from $2.8\mu_B$ to $3.5\mu_B$, while the value reported by those who argue against such a giant moment ranges between $2.3\mu_B$ and $2.7\mu_B$.[9,10] This situation clearly shows the difficulty involved in a determination of the phase composition. The NMR results reported here offer two critical points: (1) the ratio of Fe moments follows Eq. (5), and (2) the hyperfine coupling constant for the three sites should lie between 120 and 150 kOe/μ_B, and is closer to 120 kOe/μ_B. Hyperfine experiments cannot provide exact values for the Fe moments; however, these two points are valuable in the consideration of the reasonableness of the reported magnetization values for the $\mathrm{Fe_{16}N_2}$ phase.

Taking $A(\mathrm{Fe_{16}N_2})=120$ kOe/μ_B and using Eq. (5), the present NMR measurements yield the maximum possible Fe moment values: $\mu_{\mathrm{Fe}}(4e)=2.6\mu_B$, $\mu_{\mathrm{Fe}}(8h)=2.7\mu_B$, and $\mu_{\mathrm{Fe}}(4d)=3.5\mu_B$, and an average moment $\overline{\mu_{\mathrm{Fe}}}=2.9\mu_B$. This is in agreement with the result obtained by Huang and Wallace from magnetization and XRD measurements.[6] The NMR results reported here are consistent with an average Fe moment in the range of 2.7 to $2.9\mu_B$, which is the common ground for the two points of view. The present NMR study does not support the idea of either a very low or very high average Fe moment for the $\mathrm{Fe_{16}N_2}$ phase. If we follow the claim that $\overline{\mu_{\mathrm{Fe}}}=2.3\mu_B$ in $\mathrm{Fe_{16}N_2}$,[10,11] then, from Eqs. (3) and (5), $\mu_{\mathrm{Fe}}(4e)=2.0\mu_B$, $\mu_{\mathrm{Fe}}(8h)=2.2\mu_B$, and $\mu_{\mathrm{Fe}}(4d)=2.8\mu_B$. In order to fit this low value of average Fe moment to the NMR data, the value of A has to be 150 kOe/μ_B, which, as discussed above, is unreasonably large. On the other hand, if we follow the claim that $\overline{\mu_{\mathrm{Fe}}}=3.5\mu_B$,[3] this corresponds to $\mu_{\mathrm{Fe}}(4e)=3.1\mu_B$, $\mu_{\mathrm{Fe}}(8h)=3.3\mu_B$, and $\mu_{\mathrm{Fe}}(4d)=4.3\mu_B$, and A has to be 97 kOe/μ_B, which is also unreasonable since it is significantly less than the hyperfine coupling constant for the $\mathrm{Fe^{3+}}$ ion (110 kOe/μ_B).

From the point of view of a fundamental study, the determination of the saturation magnetization for $\mathrm{Fe_{16}N_2}$ relates to the issue of whether or not an Fe atom in a metallic system can carry a moment greater than $3.0\mu_B$. In this regard, the Fe moment at the $4d$ site is of most importance. According to Eq. (5), an average Fe moment greater than $2.5\mu_B$ corresponds to a Fe($4d$) moment greater than $3.0\mu_B$ (and a value of A less than 140 kOe/μ_B). Despite the large controversy over the average Fe moment among various research groups, most of the reported data implies $\mu_{\mathrm{Fe}}(4d)>3.0\mu_B$.

At first sight, it might be difficult to accept a 25% increase in the average Fe moment as a consequence of lattice enlargement. In this regard, the enhancement of the Fe moment in $R_2\mathrm{Fe}_{17}$ systems due to lattice expansion upon nitrogenation is instructive.[20] Studies of various $R_2\mathrm{Fe}_{17}$ compounds and their nitrides show that nitrogen insertion into the interstitial sites of the 2:17 phase increases the volume of the lattice by about 6%, which leads to an increase in the average Fe moment of 12–15 %.[20] In comparison with the $R_2\mathrm{Fe}_{17}$ systems, the transformation from α-Fe to $\mathrm{Fe_{16}N_2}$ leads to a volume increase of 11%. Thus one might expect a larger increase in the average Fe moment.

Finally, it should be pointed out that the giant Fe moment found in $\mathrm{Fe_{16}N_2}$ mainly originates from electron spins, and does not have a significant orbital contribution. Otherwise, as the hyperfine coupling constant for an orbital moment is much higher than that for a spin moment, one would have observed much higher Fe NMR peak frequencies.

In conclusion, the ^{57}Fe HF values for $\mathrm{Fe_{16}N_2}$ and $\mathrm{Fe_4N}$ samples have been obtained by NMR experiments. Our analysis makes use of information concerning the structural, hyperfine interaction, and magnetization data. It is shown that, in order to reconcile the magnetic data with the NMR results, the Fe atoms, especially for the $4d$ site Fe atoms, should have large atomic moments. The enhancement appears to be a volume effect. The fact that an Fe atom in Fe metallics can possess a spin moment of greater than $3.0\mu_B$ is a significant result in the field of magnetism.

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