Magnetic moment of rare earth elements in $R_2Fe_{14}B$ estimated with $\mu^+\text{SR}$

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The ferromagnetic (FM) nature of Nd$_2$Fe$_{14}$B has been investigated with muon spin rotation and relaxation ($\mu^+\text{SR}$) measurements on an aligned, sintered plate-shaped sample. A clear muon spin precession frequency ($\nu_{\mu\text{SR}}$) corresponding to the static internal FM field at the muon site showed an order parameter-like temperature dependence and disappeared above around 582 K ($\sim T_C$). This indicated that the implanted muons are static in the Nd$_2$Fe$_{14}$B lattice even at temperatures above around 600 K. Using the predicted muon site and local spin densities predicted by DFT calculations, the ordered Nd moment ($M_{\text{Nd}}$) was estimated to be 3.31 $\mu_B$ at 5 K, when both $M_{\text{Fe}}$ and $M_{\text{Nd}}$ are parallel to the $c$-axis and $M_{\text{Fe}} = 2.1 \mu_B$. Furthermore, $M_R$ in $R_2Fe_{14}B$ with $R = Y$, Ce, Pr, Sm, Gd, Tb, Dy, Ho, Er, and Tm was estimated from $J_0$ values reported in earlier $\mu^+\text{SR}$ work, using the FM structure proposed by neutron scattering and the same muon site and local spin density as in Nd$_2$Fe$_{14}$B. Such estimations yielded $M_R$ values consistent with those obtained by the other methods.

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I. INTRODUCTION

Among many permanent magnet materials, Nd$_2$Fe$_{14}$B and related intermetallic compounds$^2$ are known to be very suitable for industrial applications, due to their high saturation magnetization ($M_s = 16$ kG), large energy product ($H_cM_s = 64$ MGOe) and relatively low cost compared with that of Sm$_2$Fe$_{17}$N$_3$$^3$. Furthermore, although the Curie temperature ($T_C$) is 592 K for Nd$_2$Fe$_{14}$B, the Nd$_2$Fe$_{14}$B phase does not decompose until 1428 K, resulting in flexibility of its synthesis process. Therefore, Nd$_2$Fe$_{14}$B and related compounds are widely used for high performance motors in many devices, electric vehicles and audio speakers.

In the ferromagnetic (FM) phase, past neutron scattering measurements suggested a collinear spin structure at room temperature$^4$, in which both Fe and Nd moments ($M_{\text{Nd}}$ & $M_{\text{Fe}}$) are aligned parallel along the [001] direction. The magnitude of the ordered $M_{\text{Fe}}$ was almost saturated even at 300 K, i.e. $\sim 2.2 \mu_B$, while $M_{\text{Nd}}$ was initially thought to be below 1 $\mu_B$$^3$. The other neutron work reported that $M_{\text{Fe}} = 2.32(3) \mu_B$ and $M_{\text{Nd}} = 2.2 \mu_B$, but the recent work revealed that $M_{\text{Fe}} = 1.9(1) \mu_B$ and $M_{\text{Nd}} = 1.5(1) \mu_B$$^6$. Then, more detailed magnetization measurements at 4 K on $R_2Fe_{14}B$ with $R = La, Y, \ldots$ revealed that $M_{\text{Fe}} = 2.1 \mu_B$$^2$, leading to $M_{\text{Nd}} = 3.2 \mu_B$. In addition, Nd-NMR measurements suggested that $M_{\text{Nd}} = 2.7 \mu_B$ at 4.2 K$^7$. An X-ray magnetic circular dichroism (XMCD) study on $R_2Fe_{14}B$$^8$ implied that the ordered $M_{R}\parallel$ are very close to the values obtained from $gJ$ of 4f electrons, where $J$ is the quantum number of the total angular momentum and $g$ is the Landé factor. This means that $M_{\text{Nd}} \sim 3.3 \mu_B$.

FIG. 1: The crystal structure of Nd$_2$Fe$_{14}$B in tetragonal symmetry with space group $P4_2/mnm$ drawn by VESTA$^{10}$. Large red and yellow spheres show Nd at two different sites, medium blue and green spheres show Fe at six different sites, and small orange spheres show B. Very small pink spheres represent the muon site (0.6744,0.8840,0) predicted by first principles calculations (see text).

Furthermore, the FM spin structure in Nd$_2$Fe$_{14}$B was found to change at 135 K($\sim T_{SR}$) due to a spin reorientation transition from a high-temperature phase with $M \parallel [001]$ to a low-temperature phase with $M$ canted along the [110] direction by magnetization measurements$^{11-14}$. Initially, a collinear FM structure with a canting angle $\theta = 30.6^\circ$ at 4.2 K was proposed based on magnetization measurements on a single crystal sample$^{15}$, where $\theta$ is the angle of $M$ from the [001] direction to the [110] direction. However, both Mössbauer$^{16}$
and XMCD\textsuperscript{17} measurements suggested a non-collinear spin structure below $T_{\text{SRT}}$. That is, $\theta_{\text{Fe}}^{\text{Moss}} = 27^\circ$ and $\theta_{\text{Nd}}^{\text{Moss}} = 58^\circ$ at 4.2 K, while $\theta_{\text{Fe}}^{\text{XMCD}} = 28^\circ$ and $\theta_{\text{Nd}}^{\text{XMCD}} = 40^\circ$ at 4.2 K. The continuation of XMCD work\textsuperscript{18} indicated the formation of a further noncollinear spin structure among the Nd moments at temperatures between 80 K and $T_{\text{SRT}}$, at which $\theta_{\text{Nd,at}} \sim 80^\circ$ and $\theta_{\text{Nd,4s}} \sim 25^\circ$.

In order to further elucidate the FM ground state of Nd\textsubscript{2}Fe\textsubscript{14}B, we need another technique sensitive to internal magnetic field(s) ($H_{\text{int}}$) in solids. Unfortunately, neutron scattering is unlikely to be useful for investigating the magnetic nature of ferromagnets, because relatively weak magnetic diffraction peaks always overlap with strong nuclear Bragg peaks. Indeed, the estimated $M_{\text{Nd}}$ with neutron ranges from 1 to 2.2 $\mu_B$\textsuperscript{4,6}, which is rather small compared with those obtained with the other techniques. On the other hand, a positive muon spin rotation and relaxation ($\mu^+\text{SR}$) provides information on the local magnetic environments at the site(s) of the implanted muons, which usually locate at the interstitial site with the minimum electrostatic potential, regardless of magnetic order and/or disorder\textsuperscript{19,20}.

In fact, immediately after the discovery of the Nd\textsubscript{2}Fe\textsubscript{14}B system, a $\mu^+\text{SR}$ experiment was performed at the Paul Sherrer Institut\textsuperscript{21,22} using powder $R_2\text{Fe}_14\text{B}$ samples with $R = Y$, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm in the temperature range between 300 and 4.2 K. The $\mu^+\text{SR}$ spectra obtained in zero external field (ZF) exhibited a clear oscillation with one precession frequency for all the samples, indicating both the formation of static FM order and a single muon lattice site. However, since it was very difficult to determine the correct muon site(s) in the lattice, the muon site was assumed to be a tetrahedral site with two Fe and two Nd nearest neighbors, based on the Mössbauer and neutron data of Nd\textsubscript{2}Fe\textsubscript{14}B\textsuperscript{19,20}. In addition, the lack of information on the local spin density at the muon site made it virtually impossible to estimate the magnitude of $M_R$. As a result, the past $\mu^+\text{SR}$ result is unlikely to be recognized as a crucial work for elucidating the magnetic ground state of Nd\textsubscript{2}Fe\textsubscript{14}B.

We have therefore attempted to measure the $\mu^+\text{SR}$ spectra for Nd\textsubscript{2}Fe\textsubscript{14}B up to above $T_C$ to know the variation of $H_{\text{int}}$ with temperature and to predict muon site(s) in the lattice with density functional theory (DFT) calculations. Using the predicted muon site and the measured local spin density at the muon site, the magnitude of $M_{\text{Nd}}$ was clearly estimated even below $T_{\text{SRT}}$. Furthermore, using the past $\mu^+\text{SR}$ data for $R_2\text{Fe}_14\text{B}$ and the predicted muon site, we have obtained a systematic change in $M_R$ with the number of $4f$ electrons in $R$.

II. EXPERIMENTAL

Aligned sintered plates of Nd\textsubscript{2}Fe\textsubscript{14}B were prepared from jet-milled fine powder with the composition of 31.8Nd-0.98B-0.10Cu-0.90Co-0.15Al-0.05Ga-66.02Fe (wt%). The mean particle size of the powder was about 6 $\mu$m. The powders were then pressed under a magnetic field of 1.8 T followed by uniaxial pressing with 15 MPa. The pressed powders were sintered at 1293-1353 K for 4 hours in vacuum ($<10^{-2}$ Pa). Finally, the sintered powder $8 \times 8 \times 8$ mm$^3$ cube was sliced into 1 mm thick plates with the aligned c-axis perpendicular to the plane. The preparation and characterization of the sintered sample are explained in more detail elsewhere\textsuperscript{24}.

The $\mu^+\text{SR}$ time spectra were measured on the M20 surface muon beam line using the LAMPF spectrometer of the CMMS facility at TRIUMF in Canada. Four plates with $8 \times 8 \times 1$ mm$^3$ were arranged onto a sample holder with their $\hat{c}$ axes parallel to the beam direction ($z$) as defined in Fig. 2. For measurements in the $T$ range between 1.8 and 300 K, the samples were attached to a low-background sample holder in a liquid-He flow-type cryostat with 0.05 mm thick Al-coated Mylar tape. For measurements in the $T$ range between 300 and 600 K, the samples were fixed onto a silver plate by a 50 $\mu$m thick titanium foil, which is sandwiched between a second silver plate with a $16 \times 16$ mm$^2$ square aperture through which incoming muons passed. For the former setup, there is essentially no background signal, while for the latter case the $\mu^+\text{SR}$ signal naturally includes a background signal from muons stopped in the surrounding silver plate.

The $\mu^+\text{SR}$ spectra were obtained in either zero applied field (ZF) or transverse field (TF) with four positron detectors [backward (B), forward (F), up (U) and down (D)] arranged as shown in Fig. 2. The initial direction of the muon polarization [\textbf{$S_{\mu}(0)$}] relative to the plane of the plates was set by a Wien filter spin rotator. Here TF means the applied field is perpendicular to \textbf{$S_{\mu}(0)$}, i.e. TF$\parallel y$ in this study. The experimental techniques are described in more detail elsewhere\textsuperscript{19,20}. The resulting

**FIG. 2:** (Color online) Geometry of the $\mu^+\text{SR}$ experiment in TRIUMF: four counters [backward (B), forward (F), up (U) and down (D)] detect decay positrons emitted in the $-z$, $+z$, $+x$ and $-x$ directions, respectively. The initial muon spin direction \textbf{$S_{\mu}(0)$} is in the $+x$ direction ($\parallel \hat{a}$ of the plates) for spin-rotated (SR) mode (a) or in the $-z$ direction ($\parallel \hat{c}$) for non-spin-rotated (NSR) mode (b). Thus if the internal magnetic field ($H_{\text{int}}$) is parallel to $\hat{c}$, only U and D counters will detect a muon spin oscillation, and that only in SR mode; but if $H_{\text{int}} \perp \hat{c}$, only B and F counters in NSR mode will show an oscillatory signal. Using both configurations, one can estimate the magnetic anisotropy in the sample.
\(\mu^+\text{SR} \) data were analyzed with \textit{musrfit}\textsuperscript{25}.

The distributions of electrostatic potential and local spin density were predicted by DFT calculations with a generalized gradient approximation (GGA) plus on-site Coulomb interaction (U), as described in Sec. III B.

III. RESULTS

A. \(\mu^+\text{SR}\)

Figure 3 shows the ZF-\(\mu^+\text{SR} \) time spectra for the sintered align \(\text{Nd}_2\text{Fe}_{14}\text{B} \) plate sample recorded at (a) 300 K and (b) 2 K in two different configurations: a non-spin-rotated (NSR) mode \(|S_\mu(0)\parallel\hat{c}| \) shown in red and a spin-rotated (SR) mode \(|S_\mu(0)\perp\hat{c}| \) shown in green. The solid lines represent the best fits using Eq. (1).

\[
A_0P_{ZF}(t) = A_{FM}\exp(-\lambda_{FM}t)\cos(\omega_{FM}t + \phi_{FM}) + A_{tail}\exp(-\lambda_{tail}t).
\]

Here \(A_0\) is the initial asymmetry, \(P_{ZF}(t)\) is the muon spin depolarization function in ZF, \(A_{FM}\) and \(A_{tail}\) are the asymmetries associated with the two signals, \(\lambda_{FM}\) and \(\lambda_{tail}\) are their exponential relaxation rates, \(\omega_{FM}(\equiv \omega_{\mu}/2\pi)\) is the muon Larmor frequency corresponding to the quasi-static internal FM field, and \(\phi_{FM}\) is the initial phase. At each temperature, the two spectra were fitted using common \(\lambda_{FM}\) and \(f_{FM}\).

Such fits yielded \(A_{FM}^{S\parallel c} = 0.208(7)\), \(A_{FM}^{S\perp c} = 0.021(5)\), \(\lambda_{FM} = 30.6(1.3)\ \mu\text{s}^{-1}\), \(f_{FM} = 153.3(2)\ MHz\), \(\phi_{FM}^{S\parallel c} = \) \(\phi_{FM}^{S\perp c} = \ldots\)

Figure 4: (color online) The temperature dependences of (a) the muon spin precession frequency \(f_{FM}\), (b) the magnification of the \(f_{FM}(T)\) curve to show the anomaly at around 135 K, (c) the exponential relaxation rate \(\lambda_{FM}\), and (d) the ratio between \(\lambda_{FM}\) and \(f_{FM}\) for the \(\text{Nd}_2\text{Fe}_{14}\text{B} \) sample. The data were obtained by fitting the ZF-\(\mu^+\text{SR} \) spectrum with Eq. (1).
applied TF is very small compared with $H_{21,22}$ together with that of $f_{\text{try}}$ (combination of an exponentially relaxing cosine oscillation transition and below the vicinity of that besides the temperatures around a spin reorientation at temperatures between 150 and 550 K. This means that $T$ is almost zero below 250 K within the accuracy of $\mu^+\text{SR}$.

Figure 4 shows the temperature dependences of $f_{\text{FM}}, \lambda_{\text{FM}}$, and $\lambda_{\text{FM}}/f_{\text{FM}}$ for the Nd$_2$Fe$_{14}$B sample. The $f_{\text{FM}}(T)$ curve exhibits an order parameter-like temperature dependence and $f_{\text{FM}}$ disappears at temperatures above around 582 K ($= T_{C \text{SR}}$), which is slightly lower than $T_C$ in literatures, i.e. 592 K$^{12}$. Here it should be noted that $T_{C \text{SR}}$ is estimated from the data obtained in ZF, while the other techniques require the application of a large external magnetic field, which naturally enhances FM order. The $f_{\text{FM}}(T)$ curve also shows a sharp local maximum at 135 K ($= T_{\text{SR}}$), indicating a change in the local FM environment caused by a spin reorientation transition.

As temperature increases from 2 K, $\lambda_{\text{FM}}$ decreases slightly up to 100 K, then suddenly increases up to 150 K, and then decreases again towards $T_C$ with an increasing slope ($d\lambda_{\text{FM}}/dT$). However, below the vicinity of $T_C$, $\lambda_{\text{FM}}$ rapidly increases with temperature, and then suddenly drops to zero at $T_C$; that is, a critical behavior is observed below the vicinity of $T_C$.

It should be noted that $\lambda_{\text{FM}}/f_{\text{FM}}$, which corresponds to the normalized field distribution width, is almost temperature independent at temperatures below 100 K and at temperatures between 150 and 550 K. This means that besides the temperatures around a spin reorientation transition and below the vicinity of $T_C$; $H_{\text{int}}$ in the FM phase depends only on the magnitude of the ordered moments. These results suggest that muons are stable in the Nd$_2$Fe$_{14}$B lattice until $T_{C \text{SR}}$. The present result reproduces those in past $\mu^+\text{SR}$ work carried out below room temperature$^{21,22}$.

In order to estimate $T_C$ more correctly, Fig. 5 shows the temperature dependence of the weak transverse asymmetry ($A_{\text{TF}}$) measured with TF=50 Oe in the vicinity of $T_C$, together with that of $f_{\text{FM}}$. Here, "weak" means that the applied TF is very small compared with $H_{\text{int}}$ caused by FM order. The $wTF-$$\mu^+\text{SR}$ spectrum was fitted by a combination of an exponentially relaxing cosine oscillation due to muon spin precession in TF and Eq. (1):

$$A_0 P_{\text{TF}}(t) = A_{\text{TF}} \exp(-\lambda_{\text{TF}} t) \cos(\omega_{\text{TF}} t + \phi_{\text{TF}}) + A_{\text{FM}} \exp(-\lambda_{\text{FM}} t) \cos(\omega_{\text{FM}} t + \phi_{\text{FM}}) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t).$$

(2)

At temperatures $T \gg T_C$, $A_{\text{FM}} = A_{\text{tail}} = 0$; at temperatures $T \ll T_C$, $A_{\text{TF}} = 0$. From the middle point of a step-like change in the $A_{\text{TF}}(T)$ curve, $T_C$ is estimated as 581.57(14) K, because $A_{\text{TF}}$ is proportional to the volume fraction of paramagnetic phases in a sample. The finite value of $A_{\text{TF}}$ below $T_C$ (≈ 0.06) is from muons stopped in the surrounding silver plate.

### B. DFT calculations

First-principles calculations based on a density functional theory (DFT)$^{26,27}$ have been performed to determine the muon site in Nd$_2$Fe$_{14}$B. A self consistent field (SCF) calculation is carried out using the ultrasoft pseudopotential method$^{28,29}$, where the on-site Coulomb interaction for localized Nd-4$f$ electrons is taken into consideration using the DFT $+$ U method$^{30,31}$. The obtained pseudo SCF charge density is transformed into an all electron form with the projector augmented wave operators$^{32}$, from which the muon occupation site is estimated by the electrostatic potential analysis. The program used for the DFT calculations is an original code developed by one of the authors (K. M.), which has been successfully applied for various materials$^{33-37}$.

The cutoff energies of plane waves are set to be 25 and 200 hartrees for the pseudo wavefunctions and the charge density, respectively. The $4 \times 4 \times 4$ k-point mesh is adopted for the Brillouin zone integration. The generalized gradient approximation$^{38}$ is used for the exchange-correlation functional. The effective Coulomb and exchange parameters for Nd-4$f$ orbitals are assumed to be $U = 5$ eV$^{39}$ and $J = 0.5$ eV, respectively.

Table I shows the result of the structural relaxation in which atomic positions as well as lattice constants are fully optimized. The calculated parameters are in good agreement with the experimental ones$^{40}$. Figure 6(a) depicts the electrostatic potential: The muon site is found to be $8i$ (0.6745, 0.8838, 0) which is located near the center of a square base of a pyramid composed of Nd-3Fe-B atoms. As shown in Fig. 6(b), the spin density at the muon site is negligibly small, $\rho_{\text{spin}} = -2 \times 10^{-3} \mu_B/\text{bohr}^3$, which is eventually zero. It
should be noted that the DFT calculations with $U = 0$ provides very similar muon site and local spin density to those predicted with $U = 5$ eV. This means that the two significant parameters, i.e. the muon site and $\rho_{\text{spin}}$, are not sensitive to $U$ in the Nd$_2$Fe$_{14}$B lattice.

### TABLE I: Crystallographic parameters of ferromagnetic Nd$_2$Fe$_{14}$B

Space group: $P4_2/mnm$ (No. 136). Lattice constants: $a = 8.797$ Å, $c = 12.149$ Å (Calc.), and $a = 8.795$ Å, $c = 12.188$ Å (Expt.).

| site  | Calc.         | Expt.$^a$    |
|-------|---------------|--------------|
|       | $x$           | $y$          | $z$          |
| Nd1   | 0.2313        | 0.7687       | 0            |
| Nd2   | 0.3570        | 0.3570       | 0            |
| Fe1   | 0.0373        | 0.3599       | 0.3239       |
| Fe2   | 0.0675        | 0.2754       | 0.1270       |
| Fe3   | 0.0980        | 0.0980       | 0.2950       |
| Fe4   | 0.3180        | 0.3180       | 0.2542       |
| Fe5   | 0.0            | 0            | 0.1143       |
| Fe6   | 0.1236        | 0.1236       | 0            |
| B     | -0.25         | -0.26        |              |

$^a$Reference 40

On the contrary, the ordered magnetic moment of each element varies with $U$ (Table II). More correctly, the introduction of $U = 5$ eV reduces $M_{\text{Nd}}$ by 10%, while the change in $M_{\text{Fe}}$ is about 1%. The magnitude of $M_{\text{Fe}}$ at each site is comparable to the reported ones (see Table III). This indicates the importance of the magnitude of $U$ for estimating $M_{\text{Nd}}$ by DFT calculations.

### TABLE II: The ordered magnetic moment of each element in Nd$_2$Fe$_{14}$B predicted by DFT calculations without and with $U = 5$ eV.

| site  | GGA $M$ ($\mu_B$) | GGA+$U$ $M$ ($\mu_B$) |
|-------|------------------|-----------------------|
| Nd1   | 2.92             | 2.74                  |
| Nd2   | 3.01             | 2.72                  |
| Fe1   | 2.25             | 2.28                  |
| Fe2   | 2.20             | 2.22                  |
| Fe3   | 2.09             | 2.17                  |
| Fe4   | 2.68             | 2.68                  |
| Fe5   | 2.03             | 2.03                  |
| Fe6   | 2.32             | 2.36                  |
| B     | -0.25            | -0.26                 |

IV. DISCUSSION

#### A. Nd$_2$Fe$_{14}$B

For non-magnetized ferromagnetic materials in zero applied field, the internal magnetic field at a muon site ($H_{\mu}$) is represented by\textsuperscript{20,41-43}:

$$H_{\text{FM}} = H_{\mu}$$

![Contour plots for Nd$_2$Fe$_{14}$B in the (001) plane.](a) Electrostatic potential $\Phi_E$ and (b) spin density $m = \rho_{\text{spin}} = \rho^{\uparrow} - \rho^{\downarrow}$. The muon site is indicated by black circles.

This field is connected to the muon-spin precession frequencies through the muon gyromagnetic ratio $[f = H_{\gamma \mu} / (2\pi) = 0.013553 \text{ (MHz/Oe)} \times H \text{ (Oe)}]$ leading to

$$f_{\text{FM}} = f_{\mu} = f_{\text{dip}} + f_{\text{L}} + f_{\text{hf}}$$

where $H_{\text{dip}}$ is the dipolar field, $H_{\text{L}}$ is the Lorentz field, $H_{\text{hf}}$ is the hyperfine field, and $f_{\mu}$, $f_{\text{L}}$, and $f_{\text{hf}}$ are the corresponding muon spin precession frequencies. Furthermore, $H_{\text{L}}$ and $H_{\text{hf}}$ are connected to the saturated magnetization ($M_s$) and the local spin density at the muon sites ($\rho_{\text{spin}}$) as follows:

$$H_{\text{dip}} = -\frac{1}{4\pi\mu_0} \nabla \left( \frac{m \cdot r}{r^3} \right),$$

$$H_{\text{L}} = \frac{4\pi}{3} M_s.$$
More correctly, both Fe and Nd moments are thought to change from the [001] to the [110] direction towards the [110] direction from the [001] canted from the [001] direction to the [110] direction with a canting angle ($\theta$) of 27° for Fe and 55-66° for Nd; and ($c$) $\theta = 27°$ for Fe and Nd at the 4g site, but $\theta = 73-84°$ for Nd at the 4f site. In (b), a collinear FM spin arrangement — i.e. $\theta_{Fe} = \theta_{Nd} = 27°$ — is also shown with a broad black line.

$$H_{hf} = \frac{8\pi}{3} \times \rho_{spin}(r_{\mu}). \quad (5)$$

In order to estimate $H_{hf}$ ($f_{dip}$), we use the results of neutron diffraction4 and Mössbauer44 measurements for the magnitude and direction of the Fe moments. Assuming that the magnitude of the ordered $M_{Fe}$ is 2.1 $\mu_B$, $H_{hf}$ at the muon site is easily calculated as a function of the Nd moment using crystal structural data with dipole.45

We start by considering a collinear FM structure along the c-axis, that is, $M_{Fe} \parallel [001]$ and $M_{Nd} \parallel [001]$. Since $4\pi M_s = 18.5$ kOe at 5 K (see Table IV)22, $H_{hf} = (0, 0, 6.2$ kOe) from Eq. (5). Moreover, $H_{hf} = (0, 0, 0)$ because of the absence of any local spin density at the muon site. Consequently, we obtain the relationship between $|H_{\mu}| = H_{\mu}^{calc}$ and the magnitude of the Nd moment ($M_{Nd}$), as seen in Fig. 7(a). Here, the measured value of $f_{\mu}$ ($f_{exp}$) is 152.6(2) MHz at 2.2 K, which is very close to the reported value (156 MHz) at 5 K. Thus, in order to explain $H_{\mu}^{exp}$, $M_{Nd}$ is uniquely determined as 3.31 $\mu_B$. This is almost equivalent to $M_{Nd}$ estimated from magnetization measurements, i.e. $M_{Nd} = 3.2$ $\mu_B$, confirming the reliability of the predicted muon site from DFT calculations. From the data at room temperature, i.e. $4\pi M_s = 16.0$ kOe at 295 K and $H_{\mu}^{exp} = 151(2)$ MHz at 300 K, we also obtain that $M_{Nd} = 3.01$ $\mu_B$.

Although we assumed that $M_{Fe} = 2.1$ $\mu_B$, $M_{Nd}$ estimated with the above procedure is found to increase linearly with $M_{Fe}$ (see Fig. 8). On the contrary, Fig. 8 provides an acceptable range for $M_{Fe}$ as 2.0 $\leq M_{Fe} \leq 2.15$ $\mu_B$, when $M_{Nd}$ ranges between 3.0 and 3.5 $\mu_B$. Furthermore, we assumed that $M_{Fe}$ is identical for all the Fe sites. However, experimental studies and DFT calculations reported that $M_{Fe}$ at each site deviates slightly from 2.1 $\mu_B$. In order to know the effect of such deviations on the estimation of $M_{Nd}$, the relationship between $H_{\mu}$ and $M_{Nd}$ is also shown for the two cases in Fig. 7(a) and six cases in Table III. This indicates that the four estimations for $M_{Fe}$, i.e. exp2, exp3, calc2, and calc3, provide unusually large $M_{Nd}$ under the collinear FM structure along the c-axis.

By contrast, at low temperatures the spin orientation is reported to change from the [001] to the [110] direction below $T_{SRT}$ = 135 K11-14. The corresponding anomaly is clearly seen in the $f_{Fe}(T)$ and $\lambda_{Fe}(T)$ curves [Fig. 4]. More correctly, both Fe and Nd moments are thought to be canted towards the [110] direction from the [001] direction, based on both first principles calculations and Fe K-edge x-ray magnetic circular dichroism (XMCD) measurements.17 The canting angle ($\theta$) was estimated to be 27° for Fe ($\theta_{Fe} = 27°$) and 58° for Nd ($\theta_{Nd} = 58°$) at 4.2 K. Figure 7(b) shows the relationship between $H_{\mu}$ and $M_{Nd}$ for several $\theta_{Nd}$ values. The $\mu^+$ SR result clearly
excludes a collinear structure, in which $\theta_{\text{Fe}} = \theta_{\text{Nd}} = 27^\circ$, as an FM ground state. On the other hand, non-collinear structures provide a more plausible $M_{\text{Nd}}$, particularly when $\theta_{\text{Nd}} \sim 60^\circ$. If we assume that $M_{\text{Nd}} = 3.2 \mu_B$, $\theta_{\text{Nd}}$ should be $63^\circ$, which is very close to the value reported by XMC (58\%).

Dipole field calculations provide that the magnetic anisotropy at the muon site ($\Theta$) is 16 deg at temperatures below $T_{\text{SRT}}$, while $\Theta = 0$ deg at temperatures above $T_{\text{SRT}}$. Making comparison with the experimental result ($\Theta(300 \, \text{K}) = 7(4)\text{deg}$ and $\Theta(2 \, \text{K}) = 6(4)\text{deg}$), the experimental accuracy of $\Theta$ was likely to be overestimated. This is probably due to the fact that $S_{\mu}(0)$ for NSR mode is deviated from the $z$ direction by about 10 deg to eliminate the other particles in the muon beam. Nevertheless, we should note that the above estimation for $M_{\text{Nd}}$ is based only on the magnitude of $f_{\mu}$, and as a result, the estimated value is not affected by the alignment of the sample.

Another XMCD study at low temperatures\textsuperscript{18} proposed the possibility of a non-collinear spin arrangement among the Nd moments. That is, $\theta_{\text{Nd}} \sim 25^\circ$ for the Nd ions at the $4g$ site, but $\theta_{\text{Nd}} \sim 80^\circ$ for the Nd ions at the $4f$ site. Figure 7(c) shows the dependence of $H_{\mu}$ on $M_{\text{Nd}}$ as $\theta_{\text{Nd}}(4f)$ changes from 73 to 84°. The calculations also predict that $\theta_{\text{Nd}} = 82^\circ$ for $M_{\text{Nd}} = 3.2 \mu_B$, which looks consistent with the proposed arrangement. However, we should note that there are eight crystallographically equivalent muon sites (8i) in the Nd$_2$Fe$_{14}$B lattice. Moreover, such a non-collinear spin arrangement among the Nd moments produces two different $H_{\mu}$s at each $8i$ site — namely, $H_{\mu} = 11270$ Oe for four of the sites and 11655 Oe for the other four sites. Although the difference of the two $H_{\mu}$s (about 4%) is too small to observe two distinct muon precession frequencies in the ZF-$\mu^+$SR spectrum, such a split naturally increases the field distribution width, resulting in an increased relaxation rate $\lambda_{\text{FM}}$. In reality, $\lambda_{\text{FM}}$ and $\lambda_{\text{FM}}/f_{\text{FM}}$ at 2 K are smaller than those at room temperature [Fig. 4(b)]. This clearly excludes the model of a non-collinear spin arrangement among the Nd moments from the FM ground state for Nd$_2$Fe$_{14}$B. Since the $\lambda_{\text{FM}}(T)$ curve exhibits a broad maximum at around $T_{\text{SRT}}$ [see Fig. 4(b)], such a non-collinear spin arrangement among the Nd moments could appear in a limited temperature range particularly below the vicinity of $T_{\text{SRT}}$. Even for this case, the predicted $\Theta$ is the same to that for the collinear spin arrangement among the Nd moments, i.e. 16 deg. Therefore, $\Theta$ provides no crucial information on the spin arrangement in Nd$_2$Fe$_{14}$B within the present accuracy.

### B. $R_2$Fe$_{14}$B

Although we have measured $\mu^+$SR spectra only for Nd$_2$Fe$_{14}$B, both $H_{\mu}$ and $M_{\mu}$ were reported for the other $R_2$Fe$_{14}$B compounds with $R = Y, \text{Ce, Pr, Sm, Gd, Tb, Dy, Ho, Er, and Tm}$ (see Table IV)\textsuperscript{21,22}. Since 4f electrons are well localized at the $R$ site, it is reasonable to assume the same muon site in $R_2$Fe$_{14}$B as in Nd$_2$Fe$_{14}$B. Concerning the spin arrangement in the FM phase, the easy direction of magnetization at base temperature\textsuperscript{2} revealed that both $M_{\text{Fe}}$ and $M_{\text{R}}$ are parallel to the [001] direction in $R_2$Fe$_{14}$B with $R = Y, \text{Ce, Pr, Sm, Gd, Tb, Dy, Ho, and Tm}$, but they are parallel to the [100] direction in $R_2$Fe$_{14}$B with $R = \text{Sm, Er, and Tm}$. We also assume that $M_{\text{Fe}} = 2.1 \mu_B$ in $R_2$Fe$_{14}$B regardless of $R$.

Using the structural data of each compound, Fig. 9 shows the relationship between $H_{\mu}$ and $M_{\text{Fe}}$. For $Y_2$Fe$_{14}$B, $M_\mu$ is estimated to be almost zero (0.11 $\mu_B$), as expected for $Y^{3+}$. In fact, the recent photoelectron spectroscopic analysis result on Nd$_2$Fe$_{14}$B\textsuperscript{51,52} revealed that the valence state of Nd ions is very close to $3+$. While there is, to our knowledge, no XPS work on Y$_2$Fe$_{14}$B. The parabolic shape with a minimum at $M_\mu = 0$ [Fig. 9(b)]. For Sm$_2$Fe$_{14}$B, $H_{\mu}^{\text{exp}} < H_{\mu}^{\text{calc}}$ in the whole possible range of $M_{\text{Sm}}$, leading tentatively to $M_{\text{Sm}} = 0$. This implies that the FM spin structure is slightly different from the proposed one\textsuperscript{53}. For $Er_2$Fe$_{14}$B and $Tm_2$Fe$_{14}$B, there are two intersections between the $H_{\mu}^{\text{exp}}(M_{\text{R}})$ and $H_{\mu}^{\text{calc}}(M_{\text{R}})$ curves. This means that two values are available for $M_{\text{Er}}$ and $M_{\text{Tm}}$. However, neutron diffraction measurements proposed that $M_{\text{Er}}$ is antiparallel to $M_{\text{Fe}}\textsuperscript{54-56}$. Therefore, a negative value is selected for $M_{\text{Er}}$ and $M_{\text{Tm}}$, that is, $-9.94$ and $-9.54 \mu_B$, respectively.

For $Gd_2$Fe$_{14}$B, $Th_2$Fe$_{14}$B\textsuperscript{57}, Dy$_2$Fe$_{14}$B\textsuperscript{58}, and Ho$_2$Fe$_{14}$B\textsuperscript{59}, $M_{\mu}$ [001], $M_{\text{R}}$ [001], and $M_{\text{R}}$ is antiparallel to $M_{\text{Fe}}$. Indeed, $H_{\mu}^{\text{exp}}$ is reproduced only when $M_{\text{R}} < -9 \mu_B$ [Fig. 9(c)]. As a result, we obtain that $M_{\text{Gd}} = -9.48 \mu_B$, $M_{\text{Tb}} = -11.4 \mu_B$, $M_{\text{Dy}} = -12.6 \mu_B$, and $M_{\text{Ho}} = -10.3 \mu_B$.

Finally, Fig. 10 shows the relationship between $M_{\text{R}}$ and the expected magnetic moment $(gJ)$ derived from Landé $g$ factor and the quantum number of the total angular moment $(J)$ for free $R^{3+}$ ions. $M_{\text{R}}$ estimated with the magnetization measurements ($M_{\text{R}}^{\text{Mag}}$) is almost equivalent to $gJ^2$, suggesting the presence of stronger exchange field to the 4f moments than the crystal field\textsuperscript{2}. On the other hand, the slope of the $M_{\text{R}}^{\text{SR}}(gJ)$ curve estimated with $\mu^+$SR is steeper than that for the $M_{\text{R}}^{\text{Mag}}$ curve, mainly because $|M_{\mu}^{\text{SR}}| > |M_{\mu}^{\text{Mag}}|$ for the heavy rare earth elements. Although the reason for this discrepancy is not clear at present, we should note that $\mu^+$SR is very sensitive to local magnetic environments. Recently, not only for Nd$_2$Fe$_{14}$B but also for Ho$_2$Fe$_{14}$B, a non-collinear spin structure for the Ho moment is proposed with neutron using a single crystal sample\textsuperscript{59}. This implies the possibility that such non-collinear structure appears in the other $R_2$Fe$_{14}$B at low temperatures, which
would affect the magnitude of $M_{\mu}^{\mu SR}$. It would be thus an interesting subject to reconfirm the magnetic structure in $R_2$Fe$_{14}$B at low temperatures using a high quality sample. Finally, this work clearly demonstrates the unique power of a combination of $\mu^+$SR and DFT calculations for determining the magnetic moments of rare earth elements through the observation of local $H_{\text{int}}$.

V. SUMMARY

We have studied the internal magnetic field in a sintered Nd$_2$Fe$_{14}$B permanent magnet sample with a positive muon spin rotation and relaxation ($\mu^+$SR) technique, which provides microscopic magnetic information at the muon site. Combining the $\mu^+$SR data with the result of DFT calculations for predicting the muon site in the lattice, the magnitude of the ordered Nd moment was clearly estimated both for a collinear ferromagnetic structure at room temperature and a canted ferromagnetic structure at 2 K. Furthermore, a similar estimation for the ordered moment of the rare earth elements in $R_2$Fe$_{14}$B provided reasonable values consistent with those reported by magnetization and Mössbauer measurements. $\mu^+$SR has been widely used for investigating a magnetic nature in antiferromagnetic, spin-glass, and/or paramagnetic materials, in which both the Lorentz field and hyperfine field are usually zero and, as a result, the dipole field is predominant. On the contrary, the present work demonstrates that a combination of $\mu^+$SR and DFT calculations further expands the research field into ferromagnetic materials.

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TABLE IV: The internal magnetic field detected with $\mu^+\text{SR}^{22}$, the saturated magnetization$^2$, the magnetic moment of $R$ ($M_R$) estimated with $\mu^+\text{SR}$ ($M_R^{\mu\text{SR}}$), and $M_R$ proposed with magnetization measurements at 4 K ($M_R^{\text{Mag}}$), and $g_J$, where $g$ is the Landé $g$-factor and $J$ is the quantum number of the total angular momentum.

| $R_2\text{Fe}_{14}\text{B}$ | $H_\mu$ (MHz) | $H_\mu$ (kOe) | $3H_L = 4\pi M_s$ (kOe) | $M_R^{\mu\text{SR}} (\mu_B)$ | $M_R^{\text{Mag}} (\mu_B)$ | $g_J$ |
|--------------------------|----------------|---------------|--------------------------|-----------------------------|-----------------------------|------|
| La                       | 204.5          | 19.07         | 15.9                     | 0.11                        | —                           | 0    |
| Ce                       | 189.6          | 14.0          | 14.7                     | 0.66                        | —                           | 0    |
| Pr                       | 162.5          | 11.97         | 18.4                     | 2.79                        | 3.1                         | 3.20 |
| Nd                       | 152.6          | 11.26         | 18.5                     | 3.31                        | 3.2                         | 3.27 |
| Sm                       | 63.0           | 4.65          | 16.7                     | $\sim 0$                    | 1.0                         | 0.72 |
| Eu                       | —              | —             | —                        | —                           | —                           | 0    |
| Gd                       | 374.0          | 27.60         | 9.2                      | $-9.48$                     | $-6.8$                      | 7.0  |
| Tb                       | 405.2          | 29.90         | 6.6                      | $-11.4$                     | $-9.1$                      | 9.0  |
| Dy                       | 429.0          | 31.65         | 5.7                      | $-12.6$                     | $-10.1$                     | 10.0 |
| Ho                       | 388.0          | 28.60         | 5.7                      | $-10.3$                     | $-10.1$                     | 10.0 |
| Er                       | 157.2          | 11.58         | 6.6                      | $-9.94$                     | $-9.3$                      | 9.0  |
| Tm                       | 154.6          | 11.41         | 9.2                      | $-9.57$                     | $-6.7$                      | 7.0  |
| Yb                       | —              | —             | $\sim 12$                | —                           | $-4.2$                      | 4.0  |
| Lu                       | —              | —             | 14.7                     | —                           | —                           | 0    |

FIG. 10: The relationship between the magnetic moment of the rare earth element ($M_R$) and expected magnetic moments ($gJ$). For heavy rare earth elements, negative value of $gJ$ is used, because $M_R$ is antiparallel to $M_{\text{Fe}}$.  

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