



NMR/NQR Studies on Interactions between Multipoles and Conduction Electrons in Pr-Based Caged Compounds

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Doctoral Dissertation

NMR/NQR Studies on Interactions between Multipoles and
Conduction Electrons in Pr-Based Caged Compounds

January, 2017

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Abstract

The f electron systems have multiple degrees of freedom, e.g. the spin degree of freedom and f -orbital degrees of freedom. In many studies carried out so far, the magnetic dipole degree of freedom has been mainly focused. For an f electron occupying the highly symmetric position in the crystal, the large spin-orbit coupling and relatively small crystal electric field (CEF) acting on the f electron lead the degeneracy of its electronic state that have anisotropic charge and/or spin distributions. Such anisotropic distributions are characterized by the multiple moments and called the electric/magnetic multipoles. In the system which have the space inversion symmetry, 2^n -electric multipoles (monopole, quadrupole, hexadecapole, ...) and 2^{n+1} magnetic multipoles (dipole, octupole, triakontadipole, ...) ($n = 0, 1, 2, \dots$) can be active.

Theoretically, it is pointed out that the interaction between electric quadrupoles and conduction electrons (quadrupole Kondo effect) leads to the deviation from the Landau Fermi liquid theory. To study such an interaction, the cubic Pr-based compounds have been intensively studied in which Pr ions are trivalent and the $4f^2$ configuration is realized. Such systems can have the purely multipole active Γ_3 doublet ground state. The Γ_3 doublet is inactive for the magnetic dipoles but active for two electric quadrupoles and one magnetic octupoles. However, the known Pr-based Γ_3 ground state system so far other than $\text{PrT}_2\text{X}_{20}$ compounds (T = transition metal, $X = \text{Al, Zn}$), which is the main target of this study, are not considered to have the strong interaction with conduction electrons (c - f hybridization).

Recently, the single crystal growth and bulk property measurement of $\text{PrT}_2\text{X}_{20}$ compounds is successively reported by Onimaru *et al.* at Hiroshima University, by Sakai *et al.* at Institute for Solid State Physics, The University of Tokyo, and by Higashinaka *et al.* at Tokyo Metropolitan University. In these systems, Pr ions occupy the highly symmetric T_d position and are surrounded by $16X$ ions forming a caged structure. The ground state of $4f$ electrons in these systems is considered to be the Γ_3 doublet and the strong c - f hybridization is suggested owing to the caged structure. At high temperatures above 40 K, $\text{PrT}_2\text{Al}_{20}$ show the magnetic Kondo effect. The emergence of the Kondo effect in Pr-based compounds is unusual because, in general, $4f^2$ electrons in Pr compounds are strongly localized. The Kondo effect observed in $\text{PrT}_2\text{Al}_{20}$ implies that the c - f hybridization is strong in these compounds. At low temperatures around 1 K, $\text{PrT}_2\text{X}_{20}$ show the quadrupole order, indicating that the multipoles remain active at low temperatures. In addition, many of $\text{PrT}_2\text{X}_{20}$ show the anomalous metallic behaviors (NFL behaviors) at around 1 K. These NFL behaviors are considered to originate from the quadrupole Kondo effect. From these experimental facts, $\text{PrT}_2\text{X}_{20}$ are considered to be the ideal system to study the quadrupole-driven anomalous metallic behaviors and has been extensively studied

from theoretical and experimental viewpoints.

In this dissertation, we deal with two $\text{PrT}_2\text{Al}_{20}$ systems by using NMR/NQR measurements. One is $\text{PrNb}_2\text{Al}_{20}$ which shows the field-insensitive NFL behaviors below 10 K without clear long-range order. In this compound, the emergence of the quadrupole Kondo effect is expected. The other target is $\text{PrTa}_2\text{Al}_{20}$ shows the quadrupole ordering below 1 K. Since $\text{PrT}_2\text{Al}_{20}$ has the multiple NMR/NQR active ligand atomic sites (one T site and three Al sites), we can expected to obtain the information of multipoles from various viewpoints through the NMR/NQR measurements. This is because, in principle, these ligand sites can couple with the multipoles of 4f electrons in different ways for each of the ligand sites. To compare these contrasting compounds, we aim to perform a systematic study of the microscopic electronic states in $\text{PrT}_2\text{Al}_{20}$.

In the following paragraph, we list the main results of this study.

1. From the magnetization analysis, the CEF ground scheme is shown to be the Γ_3 doublet and the first excited state is the Γ_4 or Γ_5 triplet. This result is consistent with the previously reported specific heat measurement.
2. We could observe the ^{93}Nb - and ^{27}Al -NMR/NQR signals in both of the compounds. Due to its caged structure, NMR/NQR spectrum in $\text{PrT}_2\text{Al}_{20}$ has very complicated structure. By considering the local symmetry of these ligand atomic sites, the observed NMR/NQR signals are identified to each of the ligand sites from the spectrum analyses. This result enable us to investigate the microscopic electronic state in $\text{PrT}_2\text{Al}_{20}$ by using the NMR/NQR measurements.
3. By using the results of spectrum analysis, the magnetic anisotropy at low temperature and high fields is revealed. From the anisotropy, the CEF schemes in $\text{PrNb}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$ are determined to be the Γ_3 doublet ground state and the Γ_5 triplet first excited state. The recent inelastic neutron diffraction measurement supports this result for $\text{PrNb}_2\text{Al}_{20}$. This result is used to analyze the magnetic fluctuations in $\text{PrT}_2\text{Al}_{20}$.
4. The ^{93}Nb - and ^{27}Al -NMR Knight shift measurements, which reflect the local static magnetic susceptibility, captures the well localized nature of 4f electrons. The hyperfine coupling constant between the nuclear spins at the ligand sites and 4f electrons is much larger than the value of the classical dipole interaction, suggesting that the contribution of the c - f hybridization is large in the $\text{PrT}_2\text{Al}_{20}$.
5. From the ^{93}Nb - and ^{27}Al -NMR longitudinal relaxation rate $1/T_1$ measurements up to 19 T, which gives us the information of low-energy magnetic excitations, it is revealed that

the magnetic fluctuations in $\text{PrT}_2\text{Al}_{20}$ come from the localized $4f$ electronic fluctuations mediated by the c - f hybridizations. From the ^{93}Nb - $1/T_1$ measurements, the development of the Kondo effect is detected. The obtained strength of the Kondo effect is smaller than typical heavy electron systems but is stronger than the other cubic Pr-based Γ_3 ground state systems. This result indicates that the Γ_3 ground state is well isolated from the excited state and the purely multipole active ground state is realized at low temperatures. In addition, the strongly interactions between multipole and conduction electrons are suggested. Below 30 K, ^{93}Nb - $1/T_1T$ in $\text{PrNb}_2\text{Al}_{20}$, which is proportional to the magnitude of the low-energy magnetic fluctuations shows the field insensitive increase beyond the localized $4f$ electron model up to 19 T, indicating the development of the emergence of the additional fluctuations at low temperatures. This enhancement might be related to the NFL behaviors in $\text{PrNb}_2\text{Al}_{20}$ observed by the bulk measurements. In contrast to this result, ^{27}Al - $1/T_1T$ in $\text{PrTa}_2\text{Al}_{20}$ suddenly decreases at around 1 K up to 19 T, suggesting the phase transition and accompanying the gap opening in the excitation spectrum of $4f$ electrons at such a high field.

6. To investigate the microscopic electronic state in $\text{PrNb}_2\text{Al}_{20}$ at low temperatures, ^{93}Nb -NQR measurements were performed down to below 0.1 K. The ^{93}Nb -NQR spectrum does not change its shape down to below 0.1 K, suggesting the absence of the long-range order. The ^{93}Nb -NQR- $1/T_1$ remains almost constant down to 0.075 K, which is related to the enhanced ^{141}Pr nuclear magnetism. Such a nuclear magnetism is inherent in the nonmagnetic $4f$ ground state. The magnitude of $1/T_1$ can be quantitatively explained by the enhanced nuclear magnetism. On the other hand, the spin-echo decay rate $1/T_2$, which is sensitive to the microscopic inhomogeneity of the electronic state as well as the low-energy fluctuations, develops below 0.5 K. NQR spectrum and $1/T_1$ show no anomaly at such a temperature. By considering the bond symmetry between Pr and Nb sites, it is revealed that the magnetic octupole fluctuations can contribute to such a development of $1/T_2$ without contributing the $1/T_1$ process. This result indicates that the development of the fluctuations of multipoles is important below 1 K. Because the magnetic octupole fluctuations occur through the interactions between electric quadrupoles and conduction electrons, namely, the quadrupole Kondo effect, it is suggested that the anomalous magnetic fluctuations observed in $\text{PrNb}_2\text{Al}_{20}$ have close relationships with the multipoles and/or strong c - f hybridizations in $\text{PrNb}_2\text{Al}_{20}$.

1 General introduction

In the systems that have well-localized f -electrons, the strong Coulomb repulsion, spin-orbit coupling and relatively small crystal electric field (CEF) act on the f -electrons. In such a case, f electrons essentially have multiple degrees of freedom, e.g., the spin degree of freedom and f -orbital degrees of freedom etc. However, in many studies carried out so far, the magnetic dipole degree of freedom has been mainly focused.

When an f electron occupies the highly symmetric position in the crystal, the f electronic state can have degeneracies that are related to the f -orbital degrees of freedom. Such a degenerated electronic state has anisotropic charge/spin distributions, which is represented by using the multipole expansions. These distributions of charge/spin are called electric/magnetic multipoles. The systems which have the inversion symmetry, electric 2^{2n} multipoles (monopoles, quadrupoles, ...) and magnetic 2^{2n+1} multipoles (dipoles, octupoles, ...) can be active.

Theoretically, the interaction between electric quadrupoles and conduction electrons leads to the non-Fermi state and the non trivial ground state [1, 2]. Such an interaction is called the quadrupole Kondo effect, because such an interaction is the analog of the magnetic Kondo effect. In addition, the interactions between multipoles and conduction electrons can lead to the fluctuations of multipoles. It is believed that the unconventional superconductivity appears from the multipole fluctuations. However, a few systems have been known in which the strong interactions between multipoles and conduction electrons are realized.

To clarify the nature of such interactions, cubic Pr-based compounds having a nonmagnetic $4f$ ground state have been studied. In these compounds, Pr ions have cubic symmetry and are trivalent. In such a case, the $4f^2$ configuration is realized and $4f$ electrons are well localized. The crystal electric field (CEF) effect lifts the degeneracy of the $J = 4$ multiplet of $4f^2$ configurations. Then, $J = 4$ multiplet splits into nonmagnetic Γ_1 singlet and Γ_3 doublet, and magnetic triplets Γ_4 and Γ_5 . It is important that these CEF states include the nonmagnetic (magnetic dipoles are inactive) but multipolar active Γ_3 doublet state. When the Γ_3 doublet is the CEF ground state, it is expected that the situation is realized in which the purely multipolar active states and conduction electron interacts. However, other than $\text{PrT}_2\text{X}_{20}$ compounds, that are the main target of this study, there are a few known compounds that have the Γ_3 ground states. Such examples are PrPb_3 [3], PrMg_3 [4, 5], PrAg_2In [6], and PrPtBi [7] though these four compounds are not considered to have strong hybridizations.

Recently, cubic Pr-based $\text{PrT}_2\text{X}_{20}$ compounds (Space group $Fd\bar{3}m$, #203, T = transition metal, $X = \text{Al, Zn}$) that have the Γ_3 ground state have been extensively studied [8]. In these compounds, 16 X ions form the so-called "Frank-Kasper cage" around a Pr ion [9]. Then, strong

c - f hybridizations are expected owing to such a high coordination number. Indeed, $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V, Nb, Ta}$) shows a logarithmic increase in the $4f$ contribution to the electric resistivity ρ_{4f} above ≈ 50 K with decreasing temperature [10, 11, 12]. Such a behavior is considered to originate from the magnetic Kondo effect owing to the interactions between the CEF excited states and conduction electrons. Only three cases, PrSn_3 [13, 14], $\text{PrFe}_4\text{P}_{12}$ [15] and $\text{Pr}_2\text{Ir}_2\text{O}_7$ [16] are reported to show the logarithmic increase in ρ other than $\text{PrT}_2\text{X}_{20}$. However, the CEF ground state in these three compounds is not the Γ_3 doublet. Therefore, $\text{PrT}_2\text{X}_{20}$ compounds are the first example so far in which the coexistence of a purely multipolar active ground state and strong c - f hybridizations is realized. Indeed, many of the $\text{PrT}_2\text{X}_{20}$ compounds deviate from the Landau Fermi liquid behavior below ≈ 10 K which might be ascribed to the quadrupole Kondo effect [8], show the quadrupole order at around 1 K, and become superconducting at around 0.1 K [8]. In addition, the hybridization strength can be controlled by changing the chemical composition in these compounds. For example, $X = \text{Al}$ systems is considered to have stronger hybridizations than in $X = \text{Zn}$ systems. Then, it is expected that we can systematically study the relationships between the strength of hybridizations and difference in physical properties from the viewpoint of the composition-difference in $\text{PrT}_2\text{X}_{20}$ systems.

In the following two sections, we briefly introduce the concept of the multichannel Kondo effect, which is believed to be realized in the $\text{PrT}_2\text{X}_{20}$ systems at low temperatures [17, 18].

1.1 Multichannel Kondo effect

In the Kondo problem, what becomes the ground state in the case the orbital degrees of freedom n and impurity spin degrees of freedom $2S$ are different? This is the multichannel Kondo problem and the case of $n = 2$ and $S = 1/2$ is the two-channel Kondo effect. Nozières and Blandin [19] discussed the Hamiltonian

$$\mathcal{H} = \sum_{n=1}^m \left[\sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k},m\sigma}^\dagger c_{\mathbf{k},m\sigma} + J \sum_{\substack{\mathbf{k}\sigma \\ \mathbf{k}'\sigma'}} c_{\mathbf{k},m\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}',m\sigma'} \cdot \mathbf{S} \right], \quad (1.1)$$

where $\sigma = (\uparrow, \downarrow)$ and m denotes the spin state and orbital state, respectively. $\boldsymbol{\sigma}$ is the Pauli matrix and $\mathbf{S}$ is the spin operator for the impurity. The exact solution of Eq.(1.1) is given in Ref. [20]. In the case of $n > 2S$ and $T \ll T_K$, temperature dependences of the electrical

resistivity ρ , susceptibility χ , and specific heat C is obtained to be

$$\rho - \rho_0 \propto (T/T_K)^{2/(n+2)} \quad (1.2)$$

$$\chi, C/T \propto \begin{cases} \ln(T_K/T) & n = 2 \\ (T/T_K)^{-(n-2)/(n+2)} & n \geq 2 \end{cases}. \quad (1.3)$$

In this model, the residual entropy S_{res} appears at $T = 0$ as

$$S_{\text{res}} = \ln \frac{\sin [(2S + 1)\pi/(n + 2)]}{\sin [\pi/(n + 2)]}. \quad (1.4)$$

In the case of the two-channel Kondo effect, $S_{\text{res}} = \ln \sqrt{2}$.

1.2 Quadrupolar Kondo effect

Cox pointed out the possibility of realization of the two-channel Kondo effect in UBe_{13} [1]. In his original argument, it is assumed that U ions are tetravalent and the $5f^2$ configuration is realized. By using this case as an example, let us briefly discuss the mechanism of the quadrupolar Kondo effect. First, we assume the CEF Γ_3 doublet is the ground state. As a CEF excited state, the Γ_4 triplet with the CEF gap Δ within the $J = 4$ multiplet is taken into consideration. In addition, other than the $5f^1$ configuration is neglected as an intermediate state. If we take Δ to infinity, the $(5f^1, J = 5/2, \Gamma_7)$ state and $(5f^2, J = 4, \Gamma_3)$ state can hybridize only via the $(J = 5/2, \Gamma_8)$ state of conduction electrons from the group theoretical considerations. In addition to the fact that the Γ_3 and Γ_8 states have quadrupole moments, Γ_8 states have spin degrees of freedom owing to the Kramers' degeneracy. Then, the interaction between the Γ_3 state of the impurity and conduction electrons can be written as

$$\mathcal{H}_{\text{QK}} = J \sum_{m=\pm} \sum_{\substack{\mathbf{k}_{\tilde{\sigma}} \\ \mathbf{k}'_{\tilde{\sigma}'}}} c_{\mathbf{k},m\tilde{\sigma}}^\dagger \boldsymbol{\sigma}_{\tilde{\sigma}\tilde{\sigma}'} c_{\mathbf{k}',m\tilde{\sigma}'} \cdot \tilde{\mathbf{S}}. \quad (1.5)$$

In Eq. (1.5), m denotes the spin degrees of freedom and the quadrupole degrees of freedom are treated as the pseudo spin $\tilde{\sigma}$.

Recently, Tsuruta and Miyake investigated the lattice version of the two-channel Kondo effect by using the two-channel Anderson lattice model [21]. In their theory the ground state of f^2 configuration is the Γ_3 doublet which is connected with the Γ_7 excited state of the f^1 configuration through the hybridization with the Γ_8 conduction electrons which is similar to the

Cox's argument. They found that their model shows the NFL behaviors in a series of physical quantities at low temperatures of $10^{-3}T_K \lesssim T \lesssim 10^{-2}T_K$, where T_K is the Kondo temperature of the model. They obtained the temperature dependence of these physical quantities as [21]

Physical quantity	Temperature dependence
ρ	$\rho_0 + 1/(\text{const.} + T_K/T)$
χ	$\chi_0 - \sqrt{T/T_K}$
C	$C_0 - \sqrt{T/T_K}$

Table 1.1: Temperature dependence of the physical quantities at low temperatures in the two-channel Anderson lattice model [21].

This model can explain the temperature dependence of the non-Fermi liquid behaviors of the bulk properties in $\text{PrT}_2\text{X}_{20}$ at around 1 K [8].

2 Basic properties of $\text{PrT}_2\text{Al}_{20}$ systems (T = transition metal)

2.1 Crystal structure of $\text{PrT}_2\text{X}_{20}$

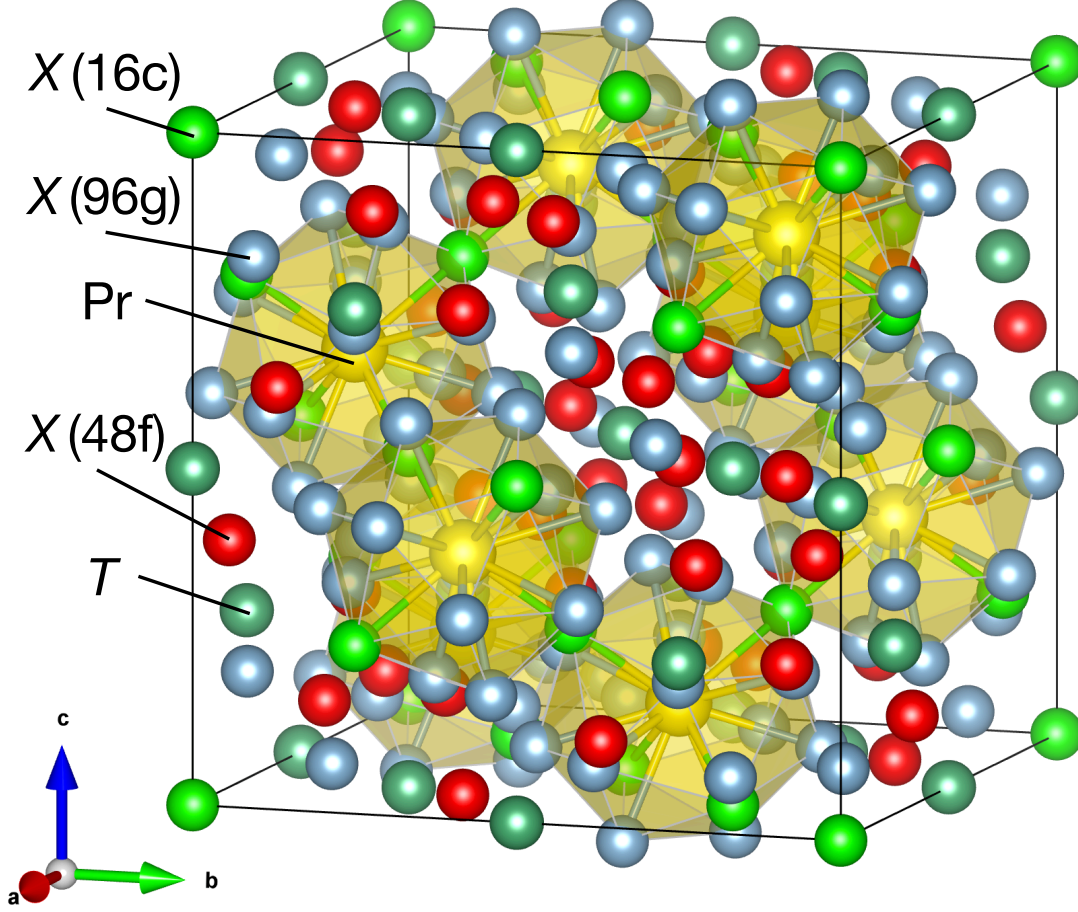


Figure 2.1: A schematic crystal structure of $\text{PrT}_2\text{X}_{20}$. This figure was drawn with VESTA 3 software [22].

Figure 2.1 shows the schematic crystal structure of $\text{PrT}_2\text{X}_{20}$, which crystallizes cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure of a space group $Fd\bar{3}m$ (#227, O_h^7). In this crystal structure, Pr ions occupy cubic T_d positions. X ions occupy three crystallographically inequivalent positions (16c, 48f, and 96g). Pr ions are encapsulated in the Frank-Kapser cage [9] formed by four X(16c) and twelve X(96g) ions. X(48f) and T ions are located outside the cage and T ions form a pyrochlore structure. The lattice constant is $a = 14.7699 \text{ \AA}$ for $\text{PrNb}_2\text{Al}_{20}$ and $a = 14.7683 \text{ \AA}$ for $\text{PrTa}_2\text{Al}_{20}$ [23].

2.2 Bulk properties of $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

2.2.1 Resistivity, susceptibility, and specific heat measurements of $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

Higashinaka *et al.* reported the synthesis of single crystal $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$) and its bulk properties at low temperatures [11, 12].

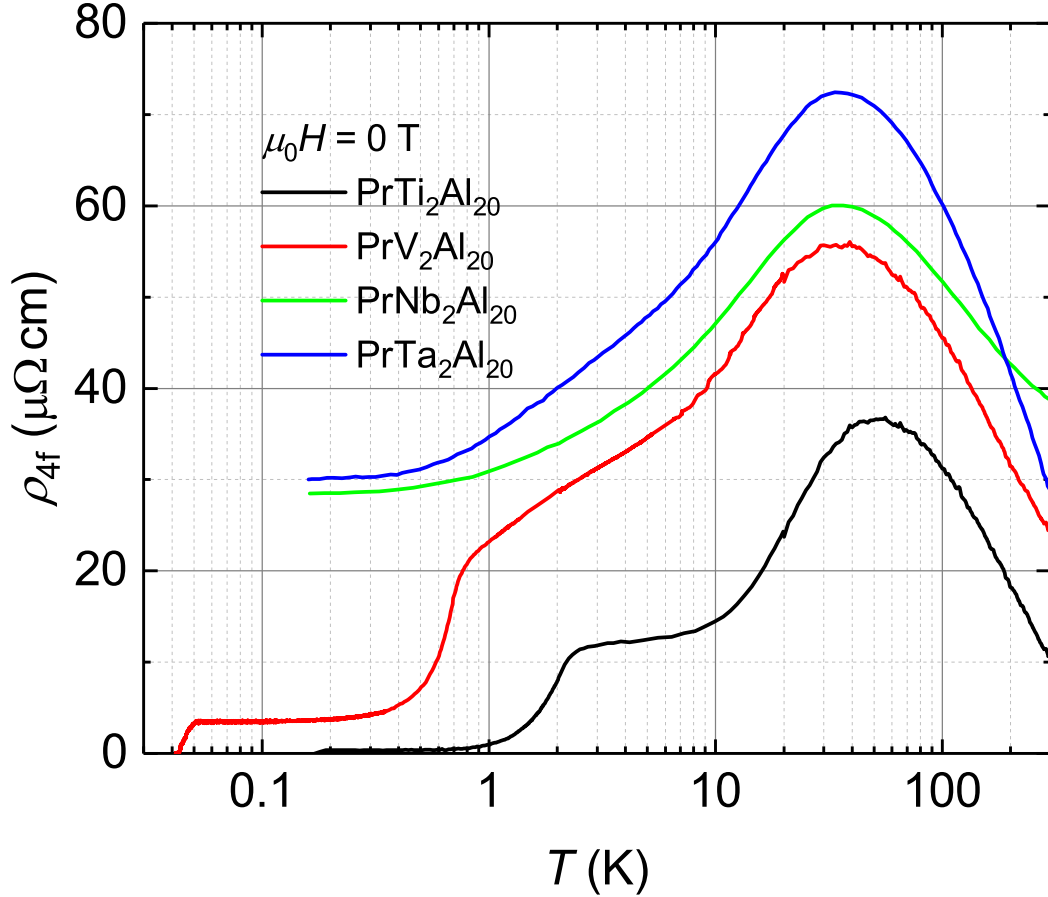


Figure 2.2: A schematic temperature dependences of the $4f$ electronic contribution for electrical resistivity ρ_{4f} in $\text{PrT}_2\text{Al}_{20}$ cited from the literatures [10, 12, 24, 25].

Figure 2.2 shows the temperature dependence of the $4f$ electronic contribution for electrical resistivity $\rho_{4f}(T)$ in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V, Nb, Ta}$). The original data is shown in Ref. [10, 12, 24, 25]. Lattice and conduction electron contributions to $\rho(T)$ are subtracted by using ρ of nonmagnetic $\text{LaT}_2\text{Al}_{20}$. Below 300 K, ρ_{4f} increases logarithmically with decreasing temperature for all of $\text{PrT}_2\text{Al}_{20}$. These behaviors are considered to originate from the magnetic Kondo effect arising from the thermally excited magnetic Γ_4 and Γ_5 triplets. ρ_{4f} shows a peak

at ≈ 55 K for $T = \text{Ti}$ and at ≈ 40 K, which may correspond to the CEF gap size between the ground and first excited states in these compounds. Below 20 K, $T = \text{Ti}$ shows Fermi liquid-like $\rho \propto T^2$ behavior, while clear deviation from $\rho_{4f} \propto T^2$ is reported for $T = \text{V}$, Nb and Ta [10, 11, 23]. ρ_{4f} in $T = \text{Ti}$ and V shows a kink related to multipole ordering. In addition, $T = \text{Ti}$ and V compounds show superconductivity below 0.2 K (Ti) and 0.05 K (V), respectively [24, 25].

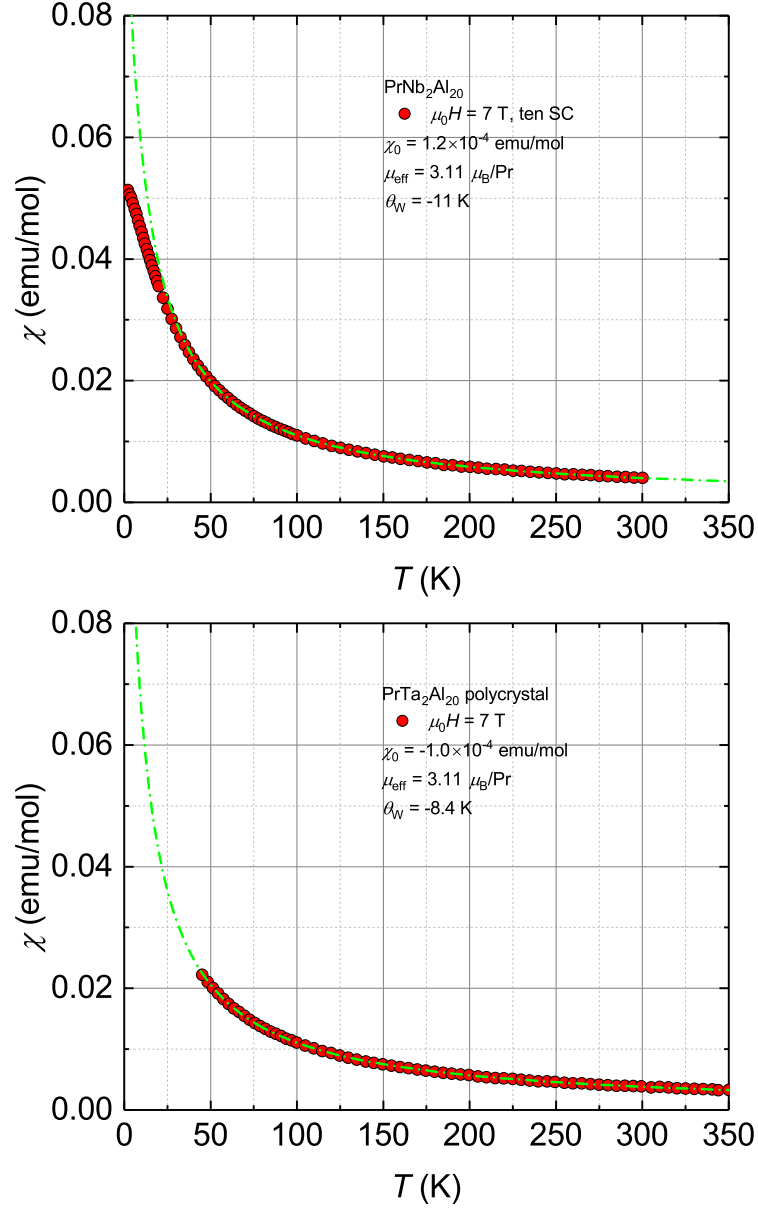


Figure 2.3: Temperature dependence of the susceptibility χ in $\text{PrNb}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$ [11, 23] measured at 7 T. The green dashed-dotted lines are the Curie-Weiss fitting above 50 K.

Figure 2.3 shows the temperature dependence of the susceptibility in (upper) χ in $\text{PrNb}_2\text{Al}_{20}$ and (lower) $\text{PrTa}_2\text{Al}_{20}$ [11, 23] obtained at 7 T. At high temperatures above 50 K, χ 's are field independent and can be fitted by the Curie-Weiss law $\chi(T) = \chi_0 + N_A \mu_{\text{eff}}^2 / 3k_B (T - \theta_W)$, where χ_0 is the temperature independent susceptibility, N_A is the Avogadro's constant, $\mu_{\text{eff}} = p_{\text{eff}} \mu_B$ is the effective Bohr magneton per Pr atom, k_B is the Boltzmann constant, and θ_W is the Weiss temperature. $\chi_0 = 1.2 \times 10^{-4}$ emu/mol, $\mu_{\text{eff}} = 3.11 \mu_B/\text{Pr}$, and $\theta_W = -11$ K are obtained for $\text{PrNb}_2\text{Al}_{20}$. $\chi_0 = -1.0 \times 10^{-4}$ emu/mol, $\mu_{\text{eff}} = 3.11 \mu_B/\text{Pr}$, and $\theta_W = -8.4$ K are obtained for $\text{PrTa}_2\text{Al}_{20}$. Below 50 K, χ 's start to saturate, indicating the CEF ground states are nonmagnetic in these compounds. The CEF gap size estimated from χ 's are about 50 K and is consistent with the result of ρ 's. p_{eff} is smaller than the ideal value of 3.58 of a free Pr^{3+} ion $J = 4$ ground state. One possible origin for such a suppression is the strong Kondo effect, which screens localized $4f$ moment. Another origin might be the CEF effect, because the fitting is performed above 200 K, we obtain $p_{\text{eff}} = 3.5 \mu_B/\text{Pr}$ for $T = \text{Ta}$. However, Pr deficiencies and/or Al substitution in the Pr site cannot be ruled out in present [11].

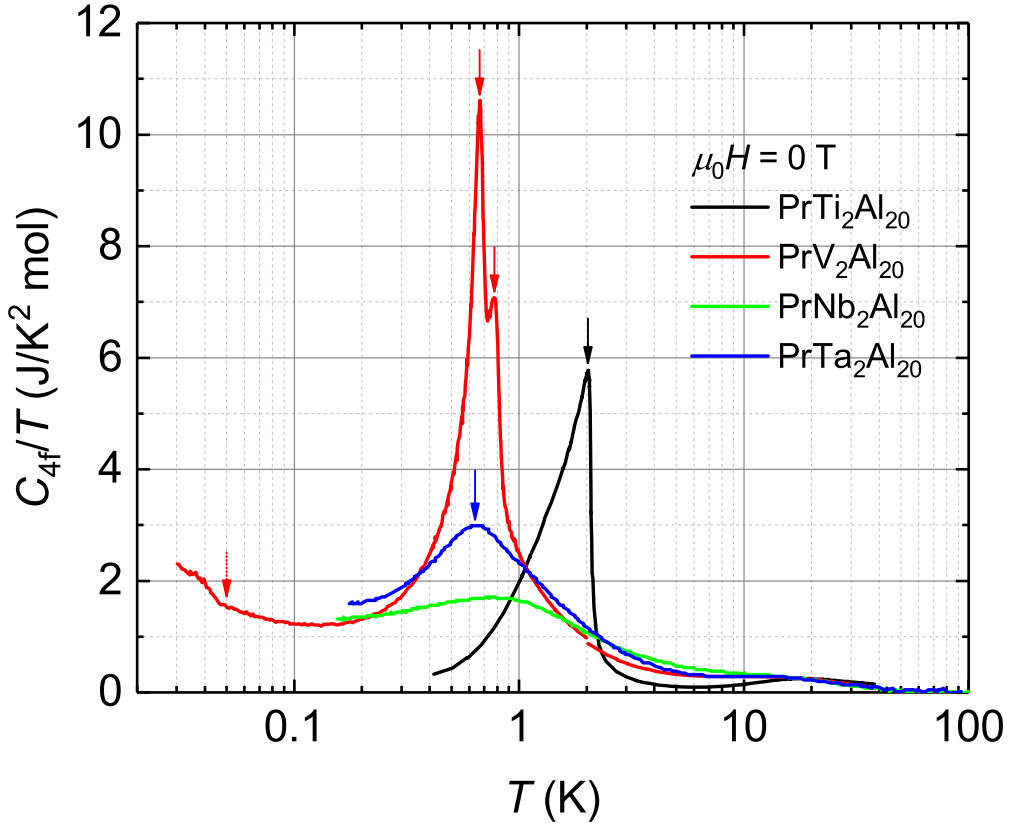


Figure 2.4: A schematic temperature dependence of the $4f$ electronic contribution for specific heat divided by temperature C_{4f}/T in $\text{PrT}_2\text{Al}_{20}$ cited from the literatures [10, 12, 25]. Quadrupole and superconducting transition temperatures are indicated by the solid and dotted arrows, respectively.

Figure 2.4 shows the schematic temperature dependence of $4f$ electronic contribution for specific heat divided by temperature C_{4f}/T in $\text{PrT}_2\text{Al}_{20}$. The original data are shown in Refs. [10, 12, 25]. Lattice and conduction electron contributions are subtracted by using C/T of nonmagnetic $\text{LaT}_2\text{Al}_{20}$. C_{4f}/T shows a broad shoulder at around 20 K for all cases of T , which might be due to the CEF excitations from the ground states to the first excited states. The CEF calculation assuming the Γ_3 ground state and Γ_4 first excited state can roughly reproduce these broad shoulders [10, 26] for $T = \text{Ti, V, Nb}$. At low temperatures around 1 K, C_{4f}/T shows a sharp peak at $T = 2.0$ K and 0.7 K for $T = \text{Ti}$ and V , respectively. These peaks are ascribed to the quadrupole order [10, 27]. In addition, a jump of C_{4f}/T due to the superconducting transition is observed at 0.05 K for $T = \text{V}$. $T = \text{Nb}$ shows no peak but a broad maximum at around 0.8 K, suggesting the strong c - f hybridizations and/or quadrupole fluctuations [12]. $T = \text{Ta}$ shows a rather sharp peak at around 0.7 K, suggesting a phase transition [12].

2.2.2 Inelastic neutron diffraction measurement for $\text{PrNb}_2\text{Al}_{20}$

Quite recently, the inelastic neutron diffraction (IND) measurement for $\text{PrNb}_2\text{Al}_{20}$ is reported by Iwasa *et al.* [26].

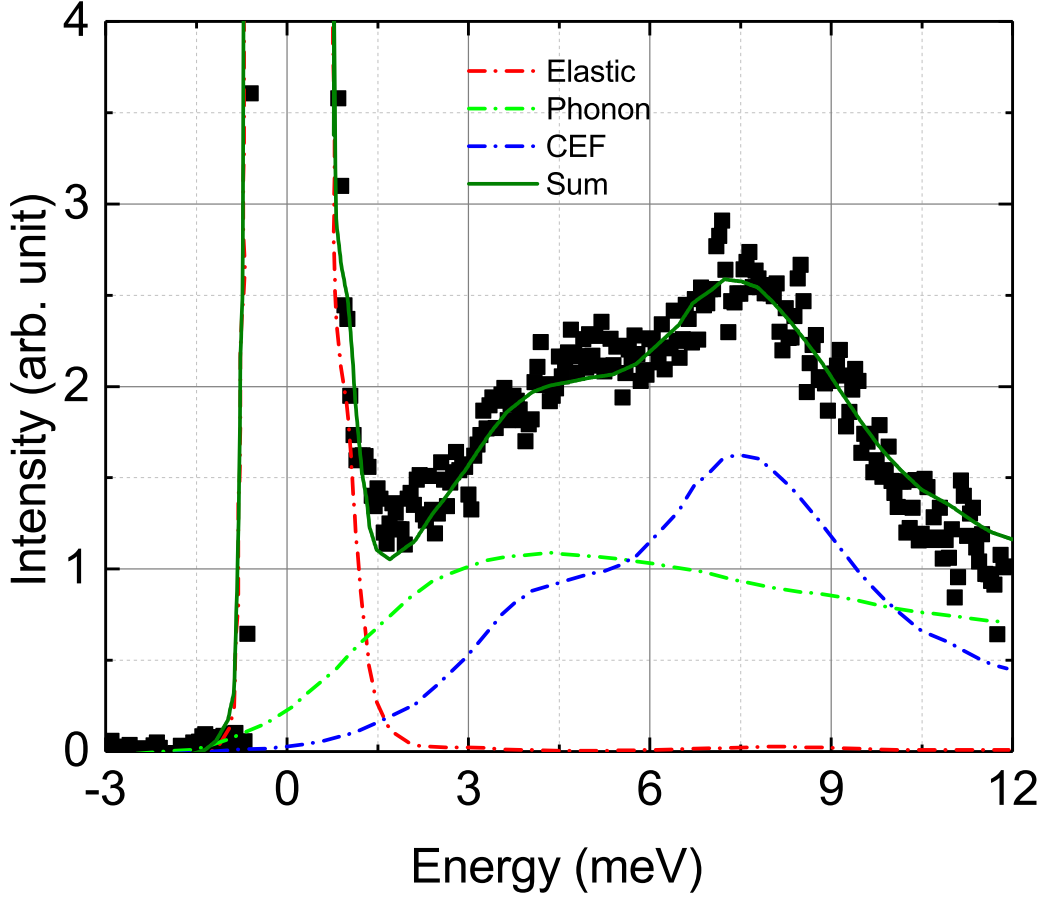


Figure 2.5: A schematic inelastic neutron spectrum of $\text{PrNb}_2\text{Al}_{20}$ obtained at 5 K. The background signal from the empty cell is subtracted. Red, light green, blue dashed-dotted lines are the calculated intensity from the elastic scattering, phonon, and $4f$ electronic crystal field excitation, respectively. A green solid line is the sum of the calculations.

Shown in Fig 2.5 is a schematic figure of the obtained IND spectrum. Original data is presented in Fig.2 of Ref.[26]. They could determined the CEF state to be Γ_3 (0 K)– Γ_5 (43.6 K)– Γ_4 (85.7 K)– Γ_1 (205.7 K) with corresponding CEF parameters to be $W = -2.87$ K and $x = -0.60$.

The remarkable feature in the IND spectrum is the broad linewidths. From their calculation, the half-width at half-maximum (HWHM) Γ_{ij} between the Γ_i and Γ_j states are estimated to be $\Gamma_{35} \approx 1.8$ meV and $\Gamma_{54} \approx 1.9$ meV. These linewidths are comparable to that of $\text{PrTi}_2\text{Al}_{20}$ [28]

and $\text{PrV}_2\text{Al}_{20}$ [29], suggesting that strong hybridizations are common features in $\text{Pr}T_2\text{Al}_{20}$ compounds. These experimental facts contrast to the sharp IND peaks in $\text{Pr}T_2\text{Zn}_{20}$ ($T = \text{Ir}, \text{Rh}$) [30].

2.2.3 Anomalous metallic state at low temperatures in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

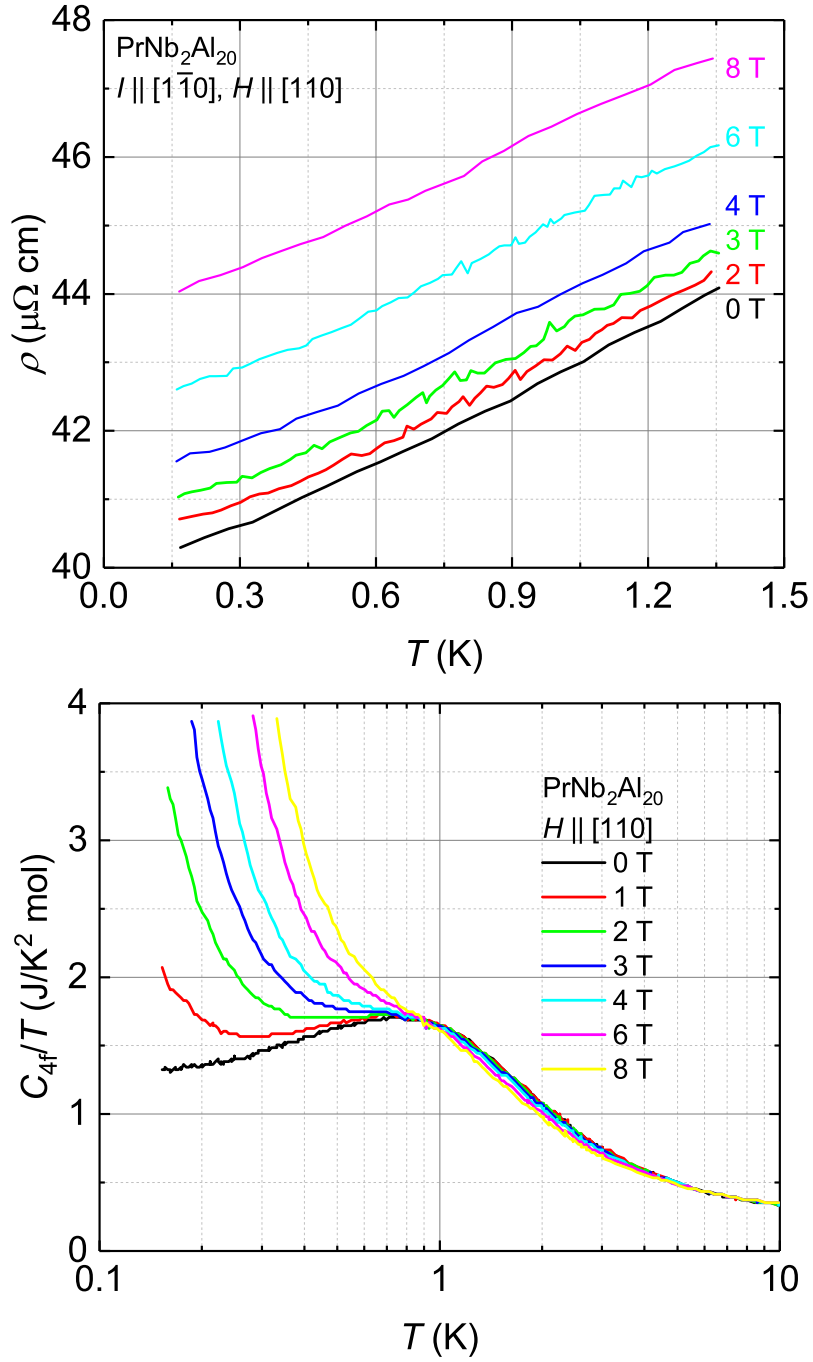


Figure 2.6: Schematic temperature and field dependences of (upper) ρ and (lower) C/T at low temperatures for $\text{PrNb}_2\text{Al}_{20}$ cited from the literature [12].

Figure 2.6 shows the schematic temperature and field dependences of ρ and C/T at low temperatures below 10 K [12]. The original data are shown in Ref. [12]. The magnetic field

is applied parallel to the $[110]$ direction. As clearly seen in the upper panel of Fig. 2.6, $\rho \approx \rho_0 + AT$ behavior is observed in $\text{PrNb}_2\text{Al}_{20}$ down to the lowest temperature of 0.15 K. In the same temperature range, C/T shows logarithmic divergence and has broad maximum at around 0.8 K as described above. The logarithmic divergence of C/T is slightly suppressed by the applied field and the peak position is almost field independent [11, 12]. Field insensitive T -linear behaviors in bulk properties suggest the nonmagnetic interactions are responsible to these NFL like behaviors.

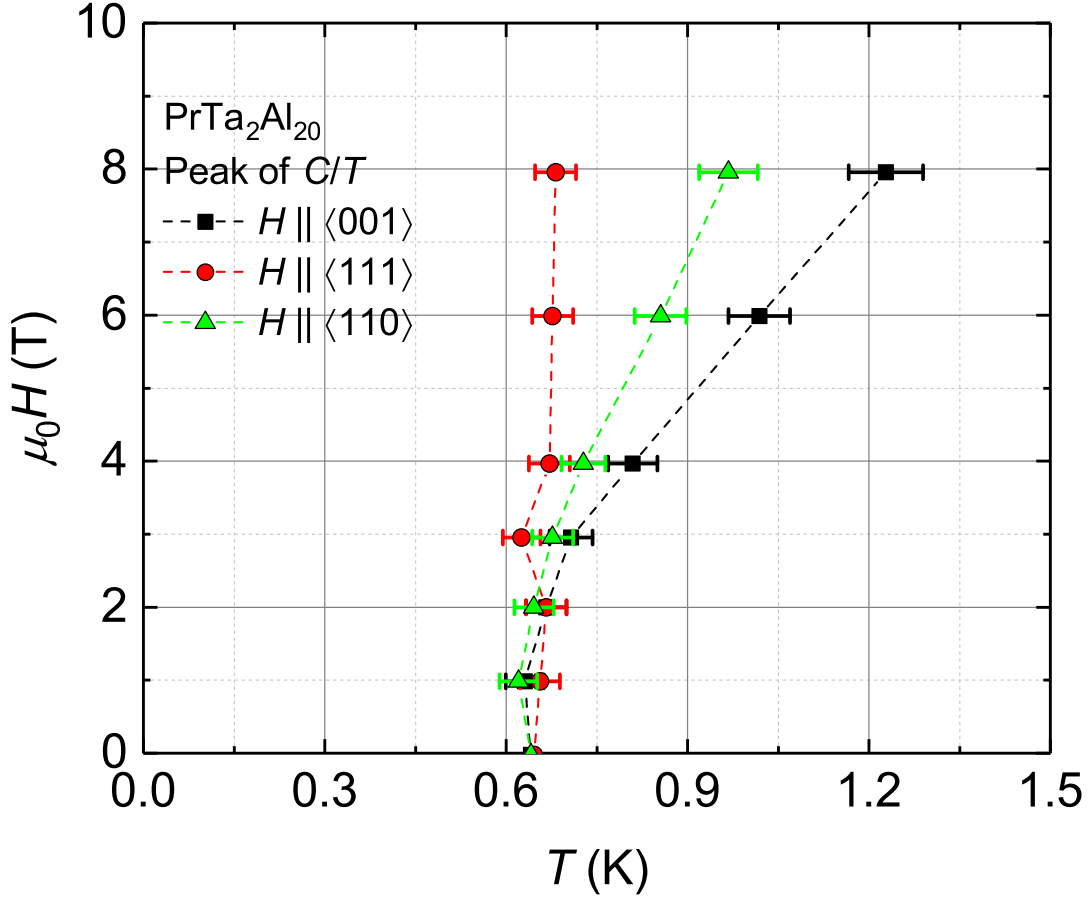


Figure 2.7: Field dependence of the C/T peak for three field directions in $\text{PrTa}_2\text{Al}_{20}$.

Figure 2.7 shows the field dependence of the peak of C/T in $\text{PrTa}_2\text{Al}_{20}$ for three field directions, $H \parallel [100]$, $[110]$ and $[111]$. At zero field, C/T has a broad peak at around 0.7 K as described above. With increasing magnetic field, the peak shifts toward high temperatures and shows an anisotropic field dependence. Such an anisotropic behavior is similar to the behaviors reported for the quadrupole ordered system such as PrPb_3 [31] and $\text{PrT}_2\text{Al}_{20}$ [10], suggesting a quadrupole order in this system. Below the peak temperature of C/T , $\rho \approx \rho_0 + AT^2$ behavior

accompanying the large residual Sommerfeld coefficient $\gamma = C/T$ and large A -coefficient is observed [12, 32]. In the same temperature range, Machida *et al.* reported the enhancement of the Seebeck coefficient S/T [32]. This enhancement is commonly observed in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V, Ta}$). The large γ , A -coefficient accompanying with the enhancement of S/T indicate the realization of mass enhancement owing to the strong c - f hybridizations.

2.2.4 Comparison with other $\text{PrT}_2\text{X}_{20}$ systems

In this section we compare the lattice and bulk magnetic properties of $\text{PrT}_2\text{X}_{20}$ systems for the comparison of c - f hybridizations in these compounds. Firstly, we list the lattice constant a , distance between Pr and X 16c sites $d_{\text{Pr-16c}}$ and between Pr and 96g sites $d_{\text{Pr-96g}}$, μ_{eff} , and θ_{W} for $X = \text{Al}$ and Zn systems [10, 11, 23, 33, 34, 35]. However, the reported θ_{W} is obtained by fitting the different temperature ranges each other. Then, to obtain the systematic comparison of θ_{W} in $\text{PrT}_2\text{X}_{20}$ systems, χ above 100 K is fitted by the Curie-Weiss law with the fixed $\mu_{\text{eff}} = 3.58\mu_{\text{B}}/\text{Pr}$ to avoid the influence of the CEF effect. The extracted Weiss temperature θ'_{W} is also listed in Table 2.2.4.

	a [Å]	$d_{\text{Pr-16c}}$ [Å]	$d_{\text{Pr-96g}}$ [Å]	μ_{eff} [μ_{B}/Pr]	θ_{W} [K]	θ'_{W} [K]
$\text{PrTi}_2\text{Al}_{20}$ [10, 33]	14.725	3.1881	3.2466	3.43	-40	-43
$\text{PrV}_2\text{Al}_{20}$ [10, 33]	14.567	3.1538	3.2183	3.57	-55	-41
$\text{PrNb}_2\text{Al}_{20}$ [11, 23]	14.7699	3.1978	3.2263	3.11	-11	-43
$\text{PrTa}_2\text{Al}_{20}$ [23]	14.7683	3.1974	3.2348	3.11	-8.4	-44
$\text{PrRh}_2\text{Zn}_{20}$ [35]	14.2702	N/A	N/A	3.55	-4.8	+4
$\text{PrIr}_2\text{Zn}_{20}$ [34]	14.2729	3.095	N/A	3.49	-2.3	-8

Table 2.1: Lattice constant a , distance between Pr and X 16c sites $d_{\text{Pr-16c}}$ and between Pr and 96g sites $d_{\text{Pr-96g}}$, and θ_{W} for $\text{PrT}_2\text{Al}_{20}$ with $X = \text{Al}$ and Zn systems. θ_{W} is obtained by analyzing χ as described in the text. N/A indicates the corresponding data is not obtained.

As can be seen in Table 2.1, $X = \text{Zn}$ systems has smaller a than $X = \text{Al}$ systems, which means smaller size of the Frank-Kasper cage. However, θ_{W} and θ'_{W} for $X = \text{Al}$ systems are much larger than that for $X = \text{Zn}$ systems, suggesting the larger exchange interactions between $4f$ electrons in $X = \text{Al}$ systems. This fact suggests not only the size of the cage, but also the ions forming the cage affect the strength of the c - f hybridization. The possible strong hybridization in $X = \text{Al}$ systems might be related with the magnetic Kondo effect observed at high temperatures. The relatively higher quadrupole transition temperature $T_{\text{Q}} \approx 0.7$ K and critical field $H_{\text{c}} \approx 10$ T in $X = \text{Al}$ systems [10, 36] than $T_{\text{Q}} \approx 0.1$ K and $H_{\text{c}} \approx 5$ T in $X = \text{Zn}$ systems [35, 37] and the broader linewidth of IND spectrum in $X = \text{Al}$ systems than in $X = \text{Zn}$

systems [26, 28, 30] are consistent with the realization of the stronger hybridization in $X = \text{Al}$ compounds than in $X = \text{Zn}$ compounds.

2.3 Purpose of the present study

In order to clarify the relationship between c - f hybridizations, multipoles, and various low temperature phenomena in $\text{PrT}_2\text{Al}_{20}$, we utilized NMR/NQR and investigated microscopic electronic states in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$). In §3, we briefly introduce the principles of NMR/NQR techniques, that can observe the microscopic electronic state around the ligand nuclei from the static and dynamical viewpoints. The NMR/NQR techniques are suitable to investigate the multipole related phenomena because, in principle, the $4f$ electronic multipoles can couple with each of the ligand nuclei in different ways and NMR/NQR can separately observe these ligand sites. In §4 and §5, we show the experimental results and discuss about the CEF states, strength of c - f hybridizations, and multipole-related low-energy magnetic excitations in $\text{PrT}_2\text{Al}_{20}$.

3 Principles of NMR and NQR

In this section, we describe the essential concepts of the nuclear magnetic resonance (NMR) and nuclear quadrupole resonance [38, 39, 40, 41].

3.1 Nuclear magnetic resonance and nuclear quadrupole resonance

The Hamiltonian $\mathcal{H}$ which describes the interactions between nuclear spins and surrounding environments can be written as:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_{\text{hf}}, \quad (3.1)$$

$$\mathcal{H}_Z = -\gamma_n \hbar \mathbf{I} \cdot \mathbf{H}_0 \quad (3.2)$$

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)} \sum_{i,j} V_{ij} \left[\frac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I(I+1) \right] \quad (3.3)$$

$$= \frac{1}{6} h\nu_Q \left[(3I_Z^2 - I(I+1)) + \frac{\eta}{2} (I_+^2 + I_-^2) \right] \quad (3.4)$$

$$\mathcal{H}_{\text{hf}} = \frac{8\pi}{3} \gamma_n \hbar g \mu_B |\phi_s(0)|^2 \mathbf{I} \cdot \mathbf{s} \quad (3.5)$$

$$- \gamma_n \hbar g \mu_B \frac{1}{r^3} \left(\mathbf{I} \cdot \mathbf{s} - \frac{3(\mathbf{s} \cdot \mathbf{r})\mathbf{r}}{r^2} \right) \quad (3.6)$$

$$+ \gamma_n \hbar \mu_B \frac{2}{r^3} \mathbf{I} \cdot \mathbf{l} \quad (3.7)$$

$$+ \sum_i \mathbf{I} \cdot \tilde{a}_{\text{hf},i} \cdot \mathbf{J}_i. \quad (3.8)$$

Equation (3.2) is the Zeeman interaction between the nuclear spin $\mathbf{I}$ and applied field $\mathbf{H}_0$, where γ_n is the nuclear gyromagnetic ratio and $\hbar$ is Dirac constant. Equation (3.3) describes the electric quadrupole interaction between the nuclear spin and the electric field gradient (EFG) $V_{ij} \equiv \partial^2 V / \partial x_i \partial x_j$ ($i, j = x, y, z$) at the nuclear position created by the surrounding charge distribution in which e is the elementary charge. $V_{i,j}$ can be diagonalized as Eq. (3.4) in its principal coordinate (X, Y, Z), where V_{ZZ} is the maximum principal value of EFG, $\eta \equiv (V_{XX} - V_{YY})/V_{ZZ}$ ($0 \leq \eta \leq 1$) is the asymmetry parameter of EFG. Equations (3.5–3.8) describe the hyperfine interaction between the nuclear spin and surrounding electrons. Equation (3.5) is the Fermi contact interaction between nuclear spin and s electron spin $\mathbf{s}$, where g is the electron g -factor, μ_B is the Bohr magneton, $|\phi_s(0)|^2$ is the probability density of s electron at the nuclear position. Equation (3.6) is the dipole interaction comes from non- s electrons. Equation (3.7) is the contribution of the orbital angular momentum of non- s electrons. Equation (3.8) comes from the total angular momentum of $4f$ electrons at $\mathbf{R}_i$. $\tilde{a}_{\text{hf},i}$

is the second rank hyperfine coupling tensor which describes the coupling between the nuclear spin and $4f$ electrons. $\tilde{a}_{\text{hf},i}$ can be decomposed as $\tilde{a}_{\text{hf},i} = \tilde{a}_{\text{dip}} + \tilde{a}_{\text{tr}}$, where $\tilde{a}_{\text{dip}}$ is the classical hyperfine coupling tensor and $\tilde{a}_{\text{tr}}$ is the transferred hyperfine coupling tensor. $\tilde{a}_{\text{dip}}$ is calculated by the lattice sum of the dipole field created by the $4f$ magnetic moment $\boldsymbol{\mu}_i = g_J \mu_B \mathbf{J}_i$:

$$\mathbf{H}_{\text{dip}} = \sum_i \mathbf{h}_{\text{dip},i} = - \sum_i \frac{1}{R_i^3} \left(\boldsymbol{\mu}_i - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{R}_i) \mathbf{R}_i}{R_i^2} \right) \quad (3.9)$$

where g_J is the Landé g -factor. Equations (3.5–3.8) can be rewritten by using the local field $\mathbf{H}_{\text{loc}}$ as:

$$\mathcal{H}_{\text{hf}} = -\gamma_n \hbar \mathbf{I} \cdot \mathbf{H}_{\text{loc}}(t) \quad (3.10)$$

$$\mathbf{H}_{\text{loc}}(t) = \langle \mathbf{H}_{\text{loc}} \rangle + \delta \mathbf{H}_{\text{loc}}(t), \quad (3.11)$$

where $\langle \mathbf{H}_{\text{loc}} \rangle$ is the expectation value and $\delta \mathbf{H}_{\text{loc}}(t)$ is the fluctuation of the local field. As discussed below, $\langle \mathbf{H}_{\text{loc}} \rangle$ determines the Knight shift and $\delta \mathbf{H}_{\text{loc}}(t)$ is the origin of the nuclear relaxation.

3.2 Knight shift

When the magnetic field $\mathbf{H}_0$ applied parallel to the z -axis, the definition of the Knight shift K in the f electron systems is

$$K \equiv \frac{\langle \mathbf{H}_{\text{loc}} \rangle_z}{H_0} = \frac{a_{\text{hf}}}{\gamma_n \hbar} \frac{\langle J_z \rangle}{H_0}, \quad (3.12)$$

where a_{hf} is the z -component of $\tilde{a}_{\text{hf}}$. By using the molar bulk susceptibility $\chi_{\text{mol}} = N_A g_J \mu_B \langle J_z \rangle / H_0$,

$$K = \frac{a_{\text{hf}}}{\gamma_n \hbar} \frac{\chi_{\text{mol}}}{N_A g_J \mu_B}, \quad (3.13)$$

where N_A is the Avogadro constant.

Experimentally, the hyperfine coupling constant A_{hf} is defined as:

$$K = \frac{A_{\text{hf}}}{N_A \mu_B} \chi_{\text{mol}}. \quad (3.14)$$

Then A_{hf} and a_{hf} are connected the following relation:

$$A_{\text{hf}} = \frac{a_{\text{hf}}}{\gamma_n \hbar g_J}. \quad (3.15)$$

3.3 Longitudinal relaxation rate $1/T_1$

Longitudinal relaxation is caused by the perturbation $\mathcal{H}'$ from the transverse component of the fluctuating internal field $\delta\mathbf{H}_{\text{loc}}(t)$. In our case, $\mathcal{H}'$ can be written as:

$$\mathcal{H}' = \sum_i \left[-\gamma_n \hbar \left(I_x \delta H_x^i + I_y \delta H_y^i \right) \right] \quad (3.16)$$

$$= \sum_i \left[-\frac{\gamma_n \hbar}{2} \left(I_+ \delta H_i^+ + I_- \delta H_i^- \right) \right], \quad (3.17)$$

where δH_i^α ($\alpha = x, y, z$) is the α -component of $\delta\mathbf{H}_i^{\text{loc}}(t)$ created by the i th spin and $\delta H_i^\pm = \delta H_i^x \pm i\delta H_i^y$. Then $1/T_1$ can be written as:

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2} \sum_i \left(\int_{-\infty}^{\infty} \langle \{ \delta H_i^x(t) \delta H_i^x(0) \} \rangle e^{-i\omega_0 t} dt + \int_{-\infty}^{\infty} \langle \{ \delta H_i^y(t) \delta H_i^y(0) \} \rangle e^{-i\omega_0 t} dt \right) \quad (3.18)$$

$$= \frac{\gamma_n^2}{2} \sum_i \int_{-\infty}^{\infty} \langle \{ \delta H_i^+(t) \delta H_i^-(0) \} \rangle e^{-i\omega_0 t} dt, \quad (3.19)$$

where ω_0 is the NMR/NQR frequency, $\langle \{AB\} \rangle = \langle (AB + BA)/2 \rangle$, and $\langle A(t)B(0) \rangle$ is the thermal average defined as:

$$\langle A(t)B(0) \rangle = \frac{\text{Tr} \{ e^{-\mathcal{H}_e/k_B T} e^{i\mathcal{H}_e t/\hbar} A e^{-i\mathcal{H}_e t/\hbar} B \}}{\text{Tr} \{ e^{-\mathcal{H}_e/k_B T} \}}, \quad (3.20)$$

where $\mathcal{H}_e$ is the hamiltonian of the electron systems.

For later convenience, we define the correlation function of the internal field $k_{\alpha\beta}^i(t)$ and its Fourier transform $K_{\alpha\beta}^i$ as:

$$k_{\alpha\beta}^i(t) = \left\langle \{ \delta H_\alpha^i(t) \delta H_\beta^i(0) \} \right\rangle \quad (3.21)$$

$$K_{\alpha\beta}^i(\omega) = \int_{-\infty}^{\infty} k_{\alpha\beta}^i(t) e^{-i\omega t} dt. \quad (3.22)$$

In the paramagnetic state, $4f$ spin fluctuation is independent from each other, namely, $k_{\alpha\beta}^i$ is independent of i , and is nonzero only for $\alpha = \beta$. $1/T_1$ can be described by using $K_{\alpha\beta}^i(\omega)$ as

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2} \sum_i \left[K_{xx}^i(\omega_0) + K_{yy}^i(\omega_0) \right]. \quad (3.23)$$

By using the Fourier transformation of $\delta\mathbf{H}_{\text{loc},i}(t)$ and the fluctuation-dissipation theorem,

$1/T_1$ can be expressed as

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \int_{-\infty}^{\infty} \left\langle \left\{ s_{\mathbf{q}}^+(t) s_{-\mathbf{q}}^-(0) \right\} \right\rangle e^{i\omega_0 t} dt \quad (3.24)$$

$$= \frac{2\gamma_n^2 k_B T}{g^2 \mu_B^2} \sum_{\mathbf{q}} A_{\mathbf{q}} A_{-\mathbf{q}} \frac{\chi_{\perp}''(\mathbf{q}, \omega_0)}{\omega_0}, \quad (3.25)$$

where $A_{\mathbf{q}} s_{\mathbf{q}}^{\pm}(t)$ is the Fourier transformation of $\delta H_i^{\pm}(t)$, and $\chi_{\perp}''(\mathbf{q}, \omega)$ is the imaginary part of the transverse component of the dynamical susceptibility $\chi = \chi' + i\chi''$. Then, $1/T_1$ gives us the information of the transverse component of the fluctuations of the internal field at the NMR frequency ω_0 .

For the case of free electrons, $\chi_{\perp}''(\mathbf{q}, \omega) \propto \rho(E_F)^2$ where $\rho(E_F)$ is the electron density of states at Fermi level, we have $1/T_1 \propto T$. For the case of localized magnetic moments, $\chi_{\perp}''(\mathbf{q}, \omega) \propto 1/T$, i.e. the Curie's law, we have $1/T_1 = \text{const.}$

3.4 Spin-echo decay rate $1/T_2$

Spin-echo decay rate $1/T_2$ can be expressed as:

$$\frac{1}{T_2} = \frac{\gamma_n^2}{2} \sum_i \left[\frac{K_{xx}(\omega_0) + K_{yy}(\omega_0)}{2} + K_{zz}(0) \right] \quad (3.26)$$

$$= \frac{1}{2T_1} + \frac{\gamma_n^2 k_B T}{g^2 \mu_B^2} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \lim_{\omega \rightarrow 0} \frac{\chi_{\parallel}''(\mathbf{q}, \omega)}{\omega}, \quad (3.27)$$

where $\chi_{\parallel}''(\mathbf{q}, \omega)$ is the longitudinal component of χ'' .

$K_{zz}(0)$ is related to the second moment of the internal field created by the nuclear spin-spin interaction and gives the Gaussian component of $1/T_{2G}$. $1/T_1$ related term gives the Lorentzian component $1/T_{2L}$.

4 Experimental

4.1 Sample preparation

Single crystal samples of $\text{PrT}_2\text{Al}_{20}$ were prepared by the Al self flux method [11]. A part of the prepared samples were crushed into the coarse grain form to obtain NMR/NQR signals at high temperatures. The obtained NQR linewidth for the coarse grain sample is not different from that of the bulk single crystals. The single crystal X-ray diffraction analysis reveals that the Nb occupancy is 0.97 for one of the $\text{PrNb}_2\text{Al}_{20}$ single crystals whereas the Pr and Al occupancies were almost unity [42]. The occupancies of Pr, Ta, and Al is almost unity for one of the $\text{PrTa}_2\text{Al}_{20}$ single crystals [23].

4.2 Experimental results

4.2.1 Magnetization measurements

The DC magnetization M is measured for the largest single crystal of $\text{PrNb}_2\text{Al}_{20}$, whose size is $\approx 1 \times 1 \times 1 \text{ mm}^3$, up to 7 T and down to 2 K by using a magnetic property measurement system (Quantum Design) at Tokyo Metropolitan University. For simplicity, the magnetic susceptibility χ is defined as $\chi \equiv M/H$ though M is generally not linear to the applied magnetic field.

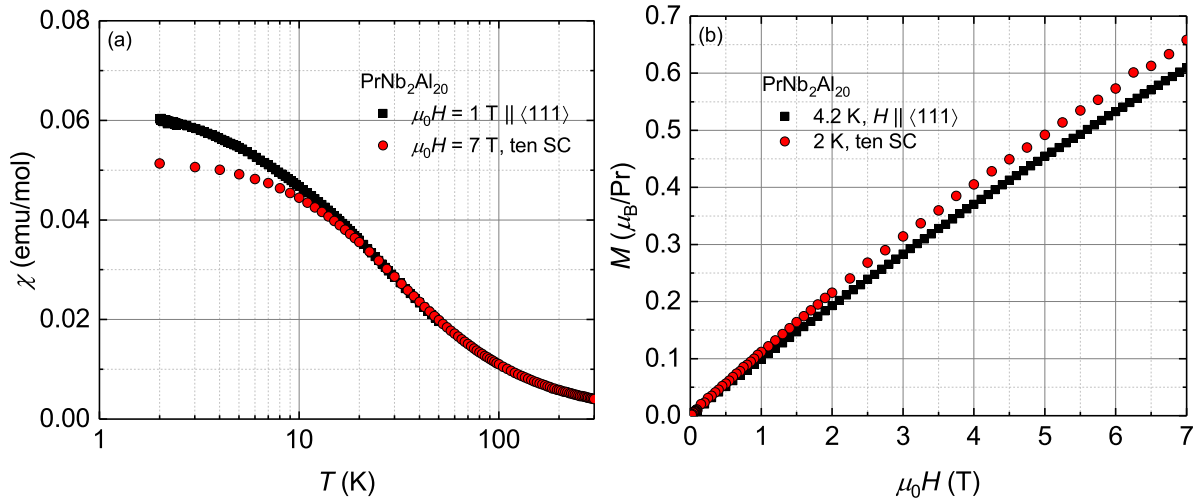


Figure 4.1:

The result is shown in Fig. 4.1 with the previously reported M and χ obtained for ten single crystals [11].

4.2.2 NMR/NQR measurement

For the NMR measurements, a commercial phase-coherent pulsed spectrometer (THAMWAY co., ltd.) and 9 T, 12 T and 17 T superconducting magnets at Kobe University were used. For the measurement above 14 T, 20 T hybrid superconducting magnet at Institute for Materials Research, Tohoku University was used. For the NMR/NQR measurement at low temperatures, a ^3He - ^4He dilution refrigerator was used down to 0.075 K.

4.2.3 NMR/NQR spectrum

The ^{93}Nb - (gyromagnetic ratio $^{93}\gamma_{\text{n}}/2\pi = 10.421 \text{ MHz/T}$, nuclear spin $I = 9/2$, nuclear quadrupole moment $Q = -0.32 \times 10^{-28} \text{ m}^{-2}$ [43, 44]) and ^{27}Al - ($^{27}\gamma_{\text{n}}/2\pi = 11.094 \text{ MHz/T}$, nuclear spin $I = 5/2$, nuclear quadrupole moment $Q = -0.1466 \times 10^{-28} \text{ m}^{-2}$ [43, 44]) NMR/NQR spectra are obtained for the coarse-grain (powder) and single crystal samples of $\text{PrNb}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$ by sweeping the frequency at the fixed magnetic field or sweeping magnetic field at the fixed frequency.

The obtained NMR/NQR spectra in $\text{PrNb}_2\text{Al}_{20}$ powder are shown in Figs. 4.2–4.4.

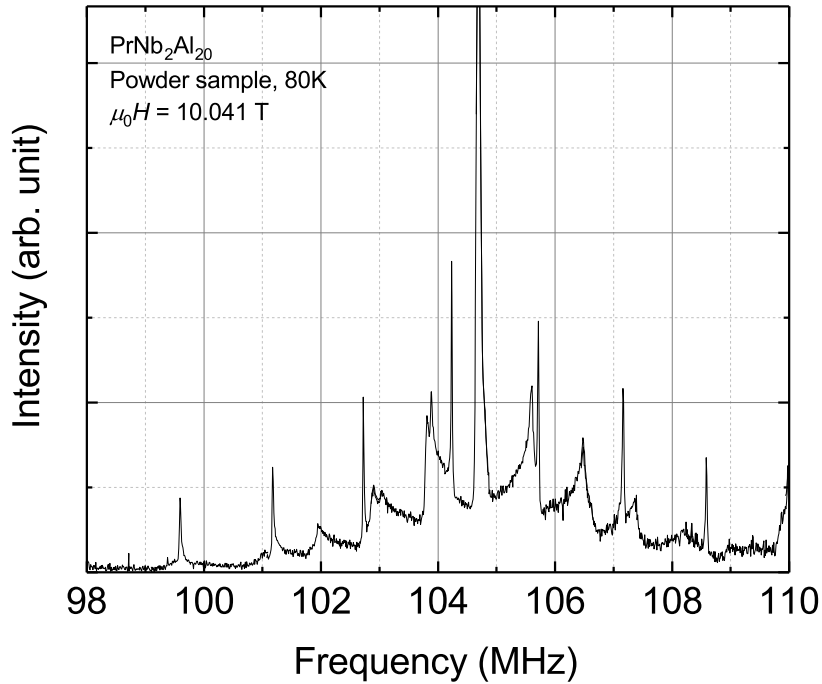


Figure 4.2: ^{93}Nb -NMR spectrum in $\text{PrNb}_2\text{Al}_{20}$ obtained at $\mu_0 H = 10.041 \text{ T}$ and at 80 K.

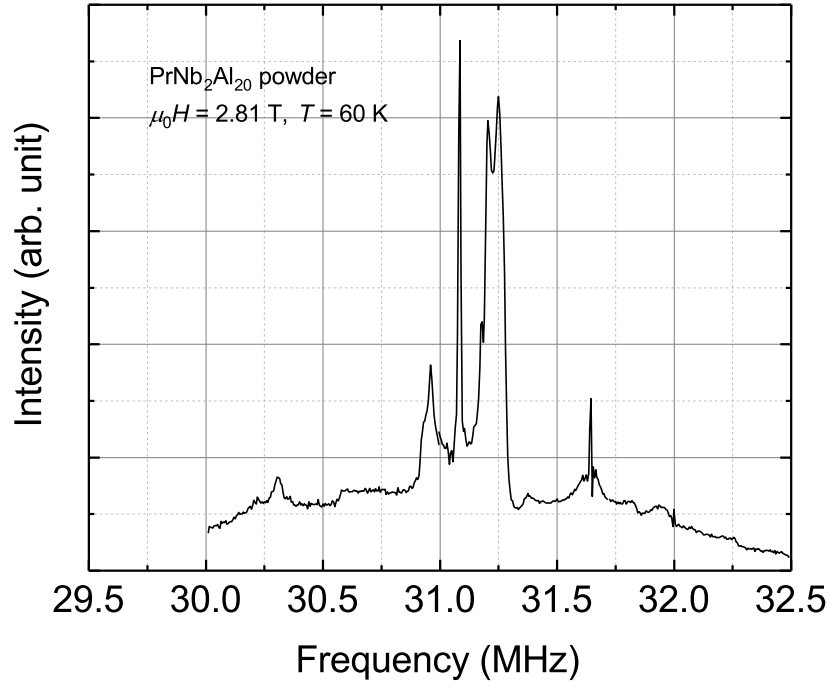


Figure 4.3: ^{93}Nb - and ^{27}Al -NMR spectra in $\text{PrNb}_2\text{Al}_{20}$ obtained at $\mu_0 H = 2.81$ T and at 60 K.

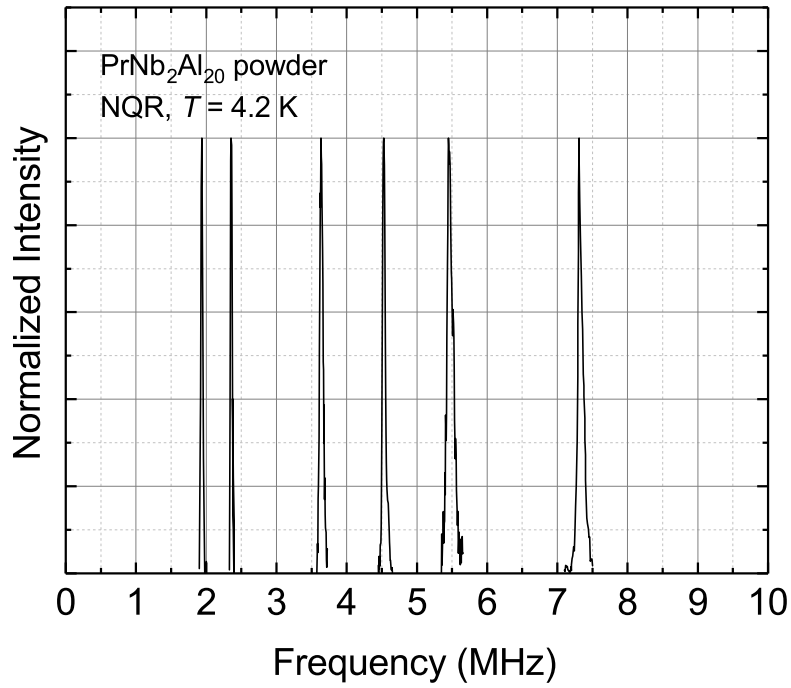


Figure 4.4: ^{93}Nb - and ^{27}Al -NQR spectrum obtained at 4.2 K.

The obtained ^{93}Nb - and ^{27}Al -NMR spectra in a $\text{PrNb}_2\text{Al}_{20}$ single crystal are shown in

Fig. 4.5. In the measurements, the magnetic field is applied parallel to one of the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions.

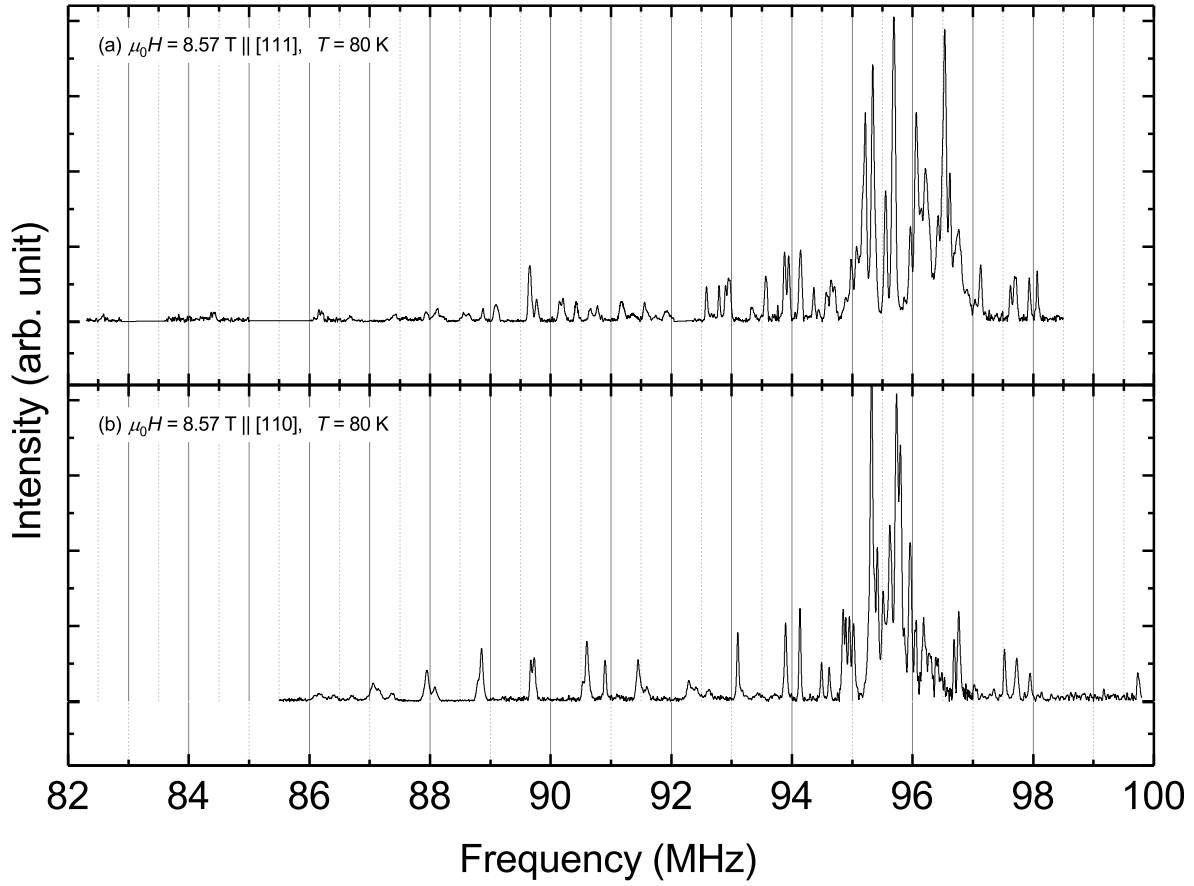


Figure 4.5: ^{93}Nb - and ^{27}Al -NMR spectrum in $\text{PrNb}_2\text{Al}_{20}$ single crystal obtained at $\mu_0 H = 8.57 \text{ T}$ and at 80 K . (a) H is applied parallel to one of the $\langle 111 \rangle$ directions. (b) H is applied parallel to one of the $\langle 110 \rangle$ directions.

The obtained spectra in $\text{PrTa}_2\text{Al}_{20}$ powder are shown in Figs. 4.6, 4.7.

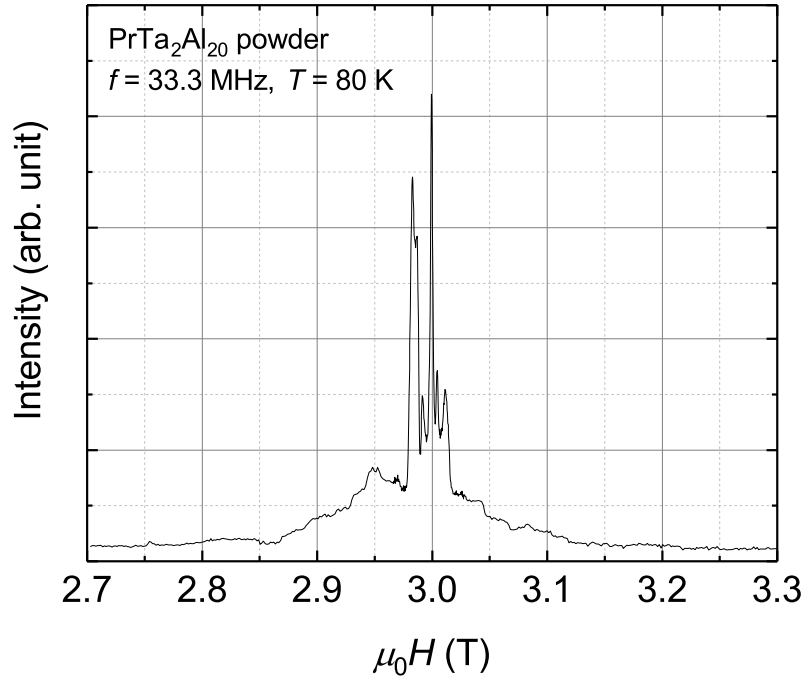


Figure 4.6: ^{27}Al -NMR spectrum in $\text{PrTa}_2\text{Al}_{20}$ obtained at $\mu_0 H = 2.81$ T and at 60 K.

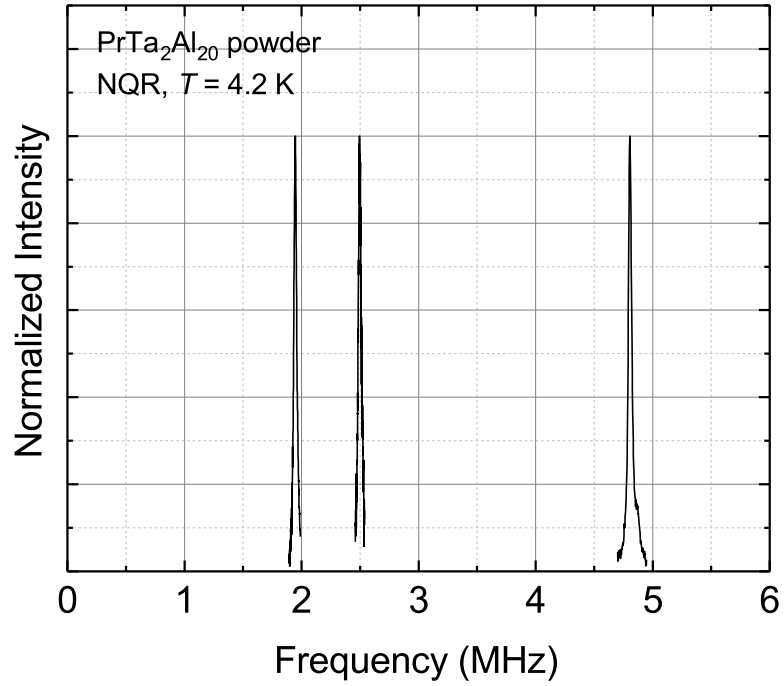


Figure 4.7: ^{27}Al -NQR spectrum in $\text{PrTa}_2\text{Al}_{20}$ obtained at 4.2 K.

4.2.4 NMR/NQR longitudinal relaxation rate $1/T_1$

Figure 4.8 shows the longitudinal relaxation curve obtained for ^{93}Nb -NMR/NQR in $\text{PrNb}_2\text{Al}_{20}$ and for ^{27}Al -NMR in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$).

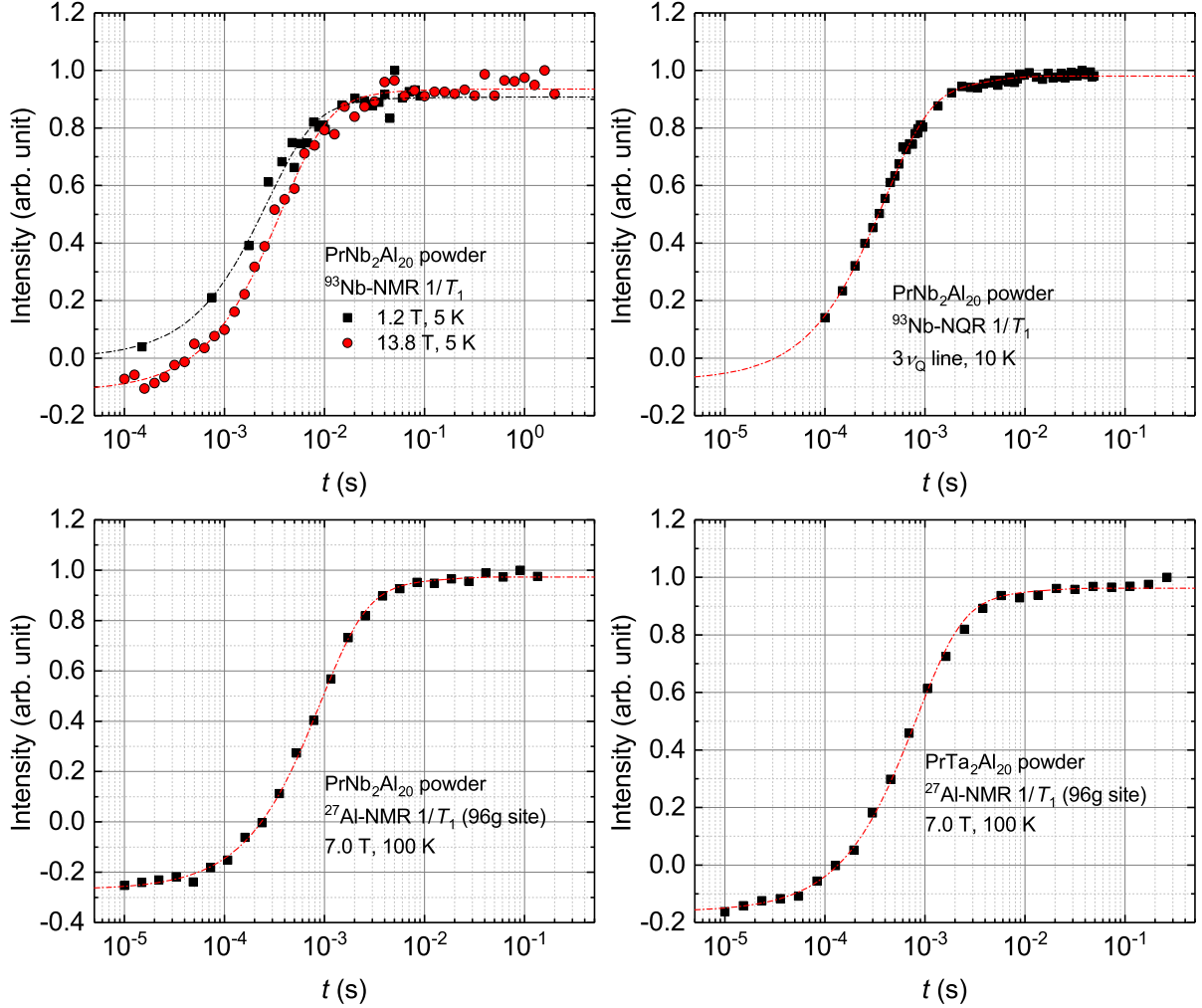


Figure 4.8: Typical recovery curves obtained for (Upper left) ^{93}Nb -NMR, (Upper right) ^{93}Nb -NQR, (Lower left) ^{27}Al -NMR in $\text{PrNb}_2\text{Al}_{20}$, and (Lower right) ^{27}Al -NMR in $\text{PrTa}_2\text{Al}_{20}$

$1/T_1$ is measured by the inversion recovery method and the spin-echo intensity is recorded as a function of the time after the inversion pulse. As an inversion pulse, a single π or $\pi/2$ pulse is used. The recovery curves are well fitted by the magnetic relaxation process as shown in Fig. 4.8 and details will be discussed in §5.4.1. For example, at the central line of ^{93}Nb -NMR spectrum (upper left figure in Fig. 4.8), For the central line of ^{93}Nb -NMR ($I = 9/2$), we fitted

the relaxation curve by using

$$\frac{M_\infty - M(t)}{M_0} = \frac{1}{165}e^{-t/T_1} + \frac{24}{715}e^{-6t/T_1} + \frac{6}{65}e^{-15t/T_1} + \frac{1568}{7293}e^{-28t/T_1} + \frac{7938}{12155}e^{-45t/T_1}, \quad (4.1)$$

where $M(t)$ is the magnetization at time t after the inversion pulse, M_∞ is the magnetization at the thermal equilibrium, M_0 is the magnetization just after the inversion pulse.

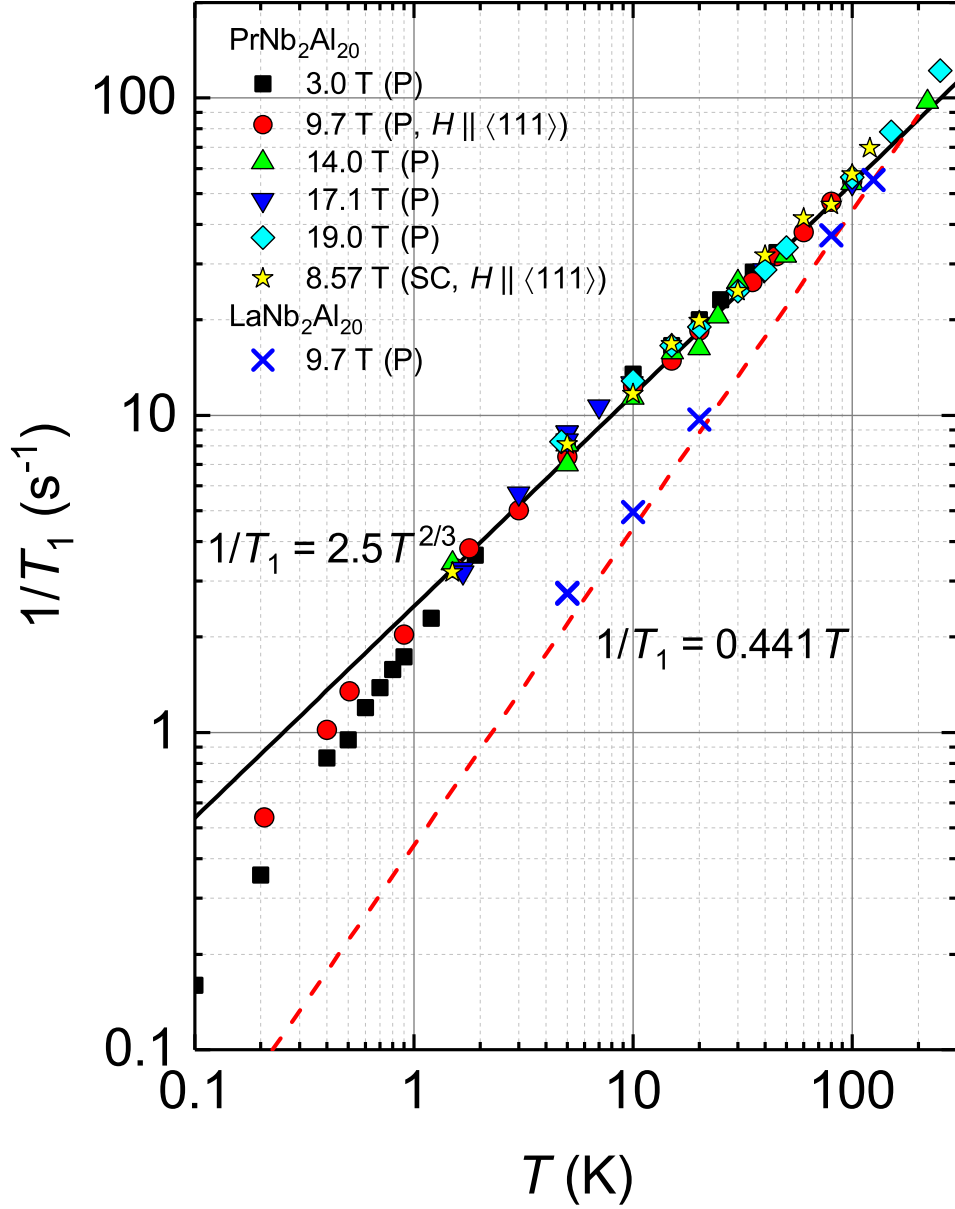


Figure 4.9: Temperature and field dependences of NMR- $1/T_1$ at Nb site in $\text{PrNb}_2\text{Al}_{20}$ and $\text{LaNb}_2\text{Al}_{20}$.

Figure 4.9 shows the temperature and field dependences of ^{93}Nb -NMR $1/T_1$ between 3 and 19 T by using powder (P) and single crystal (SC) samples. At 3 T, $1/T_1$ is measured at the second satellite line of the powder spectrum to avoid the line overlaps with ^{27}Al signals of the sample. At high fields above 3 T, all of the data was taken at the central line of the spectrum. For the measurements of a single crystal, a magnetic field was applied parallel to one of the $\langle 111 \rangle$ directions. The measurement at 9.7 T was performed using a field aligned powder sample.

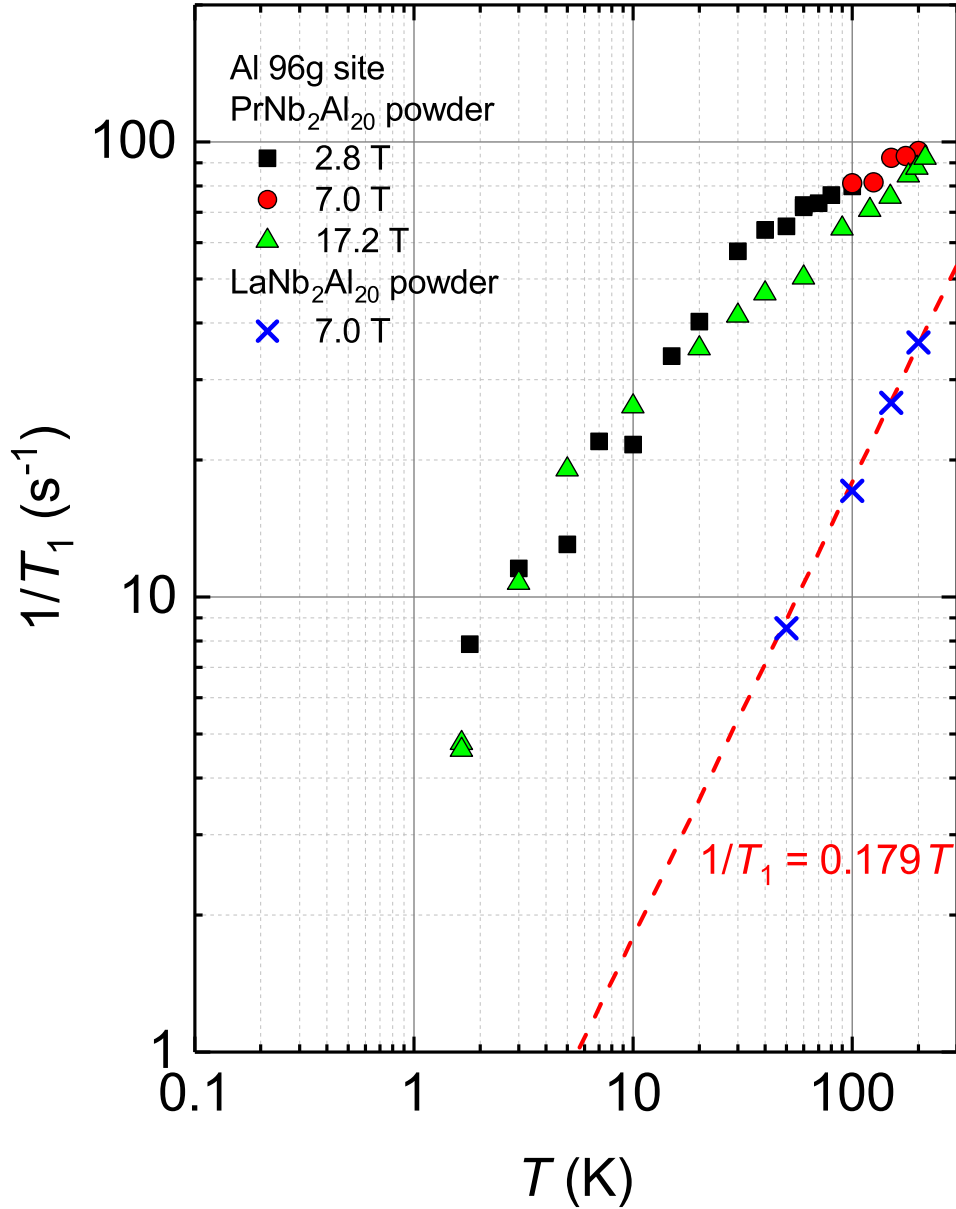


Figure 4.10: Temperature and field dependences of NMR- $1/T_1$ at Al 96g site in $\text{PrNb}_2\text{Al}_{20}$ and in $\text{LaNb}_2\text{Al}_{20}$.

Figure 4.10 shows the temperature and field dependence of $1/T_1$ obtained for Al 96g site in the powder sample of $\text{PrNb}_2\text{Al}_{20}$ between 3 and 17 T. $1/T_1$ is measured at the central line of Al 96g site and by the inversion recovery method.

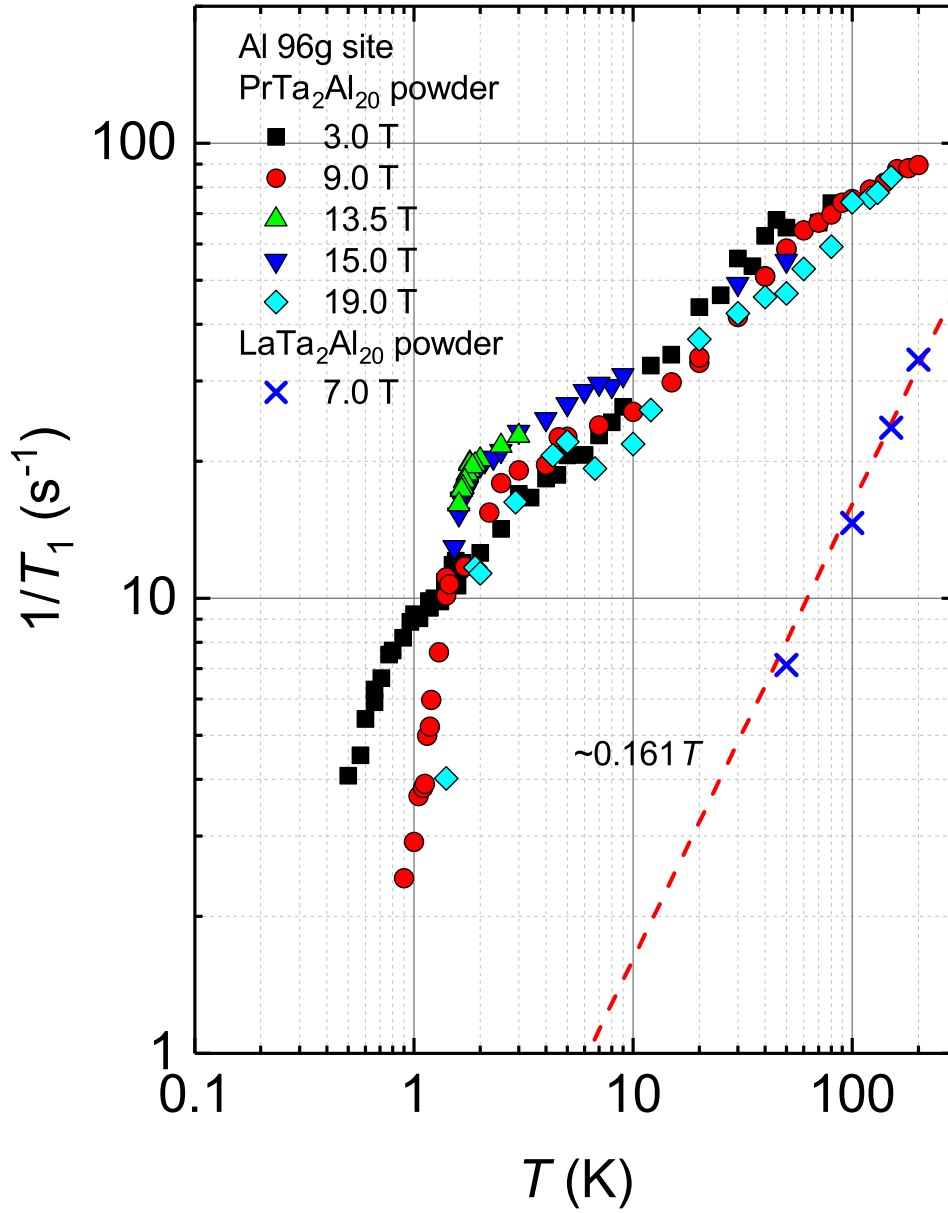


Figure 4.11: Temperature and field dependences of $1/T_1$ measured at $\text{PrTa}_2\text{Al}_{20}$ powder.

Figure 4.11 shows the temperature dependence of $1/T_1$ measured at the central line of Al 96g site in the powder sample of $\text{PrTa}_2\text{Al}_{20}$.

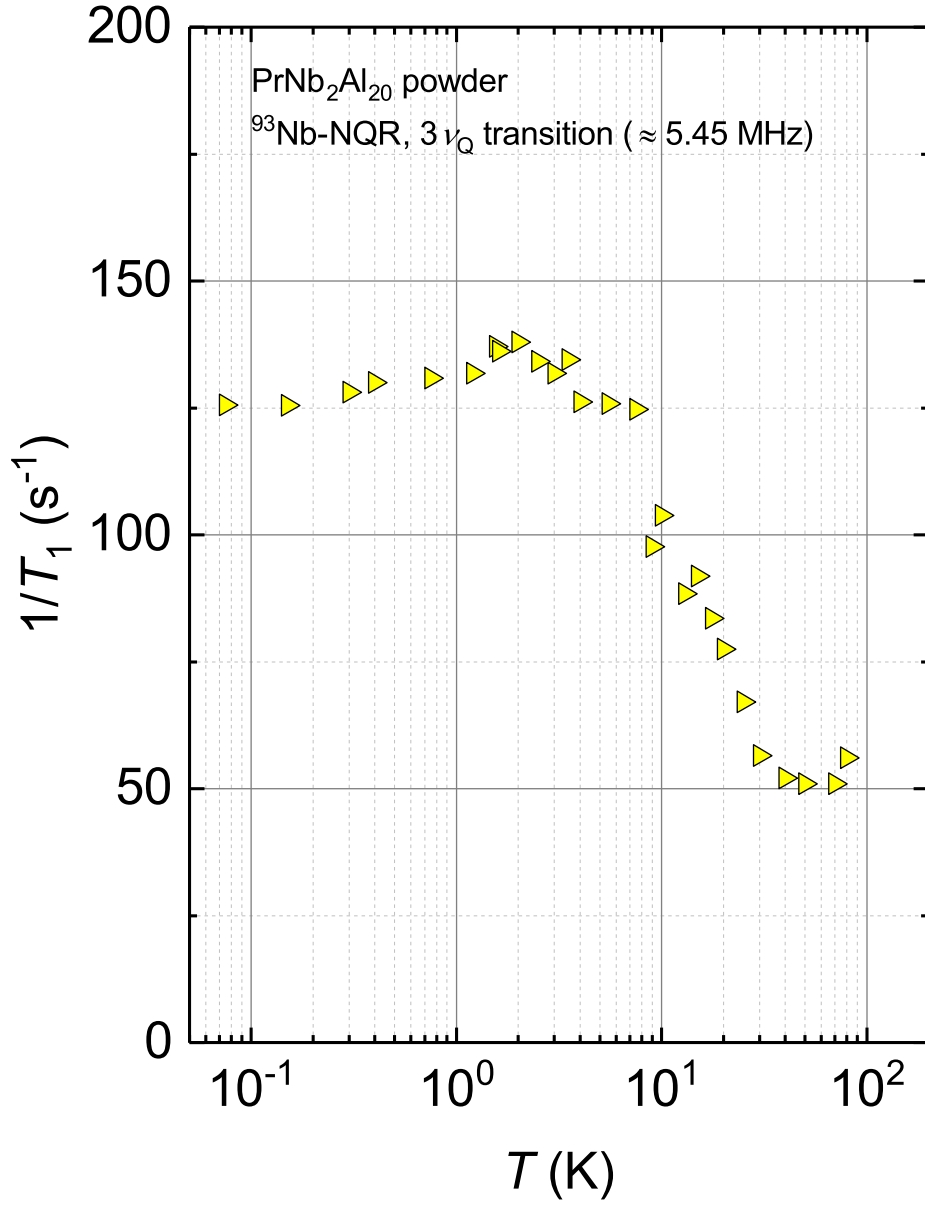


Figure 4.12: Temperature dependence of ⁹³Nb-NQR $1/T_1$ measured at NQR- $3\nu_Q$ transition (≈ 5.45 MHz) in PrNb₂Al₂₀.

Figure 4.12 displays the temperature dependence of ⁹³Nb-NQR $1/T_1$ in PrNb₂Al₂₀. Measurement is performed at $3\nu_Q$ transition (≈ 5.45 MHz) by using the inversion recovery method.

4.2.5 NQR spin echo decay rate $1/T_2$

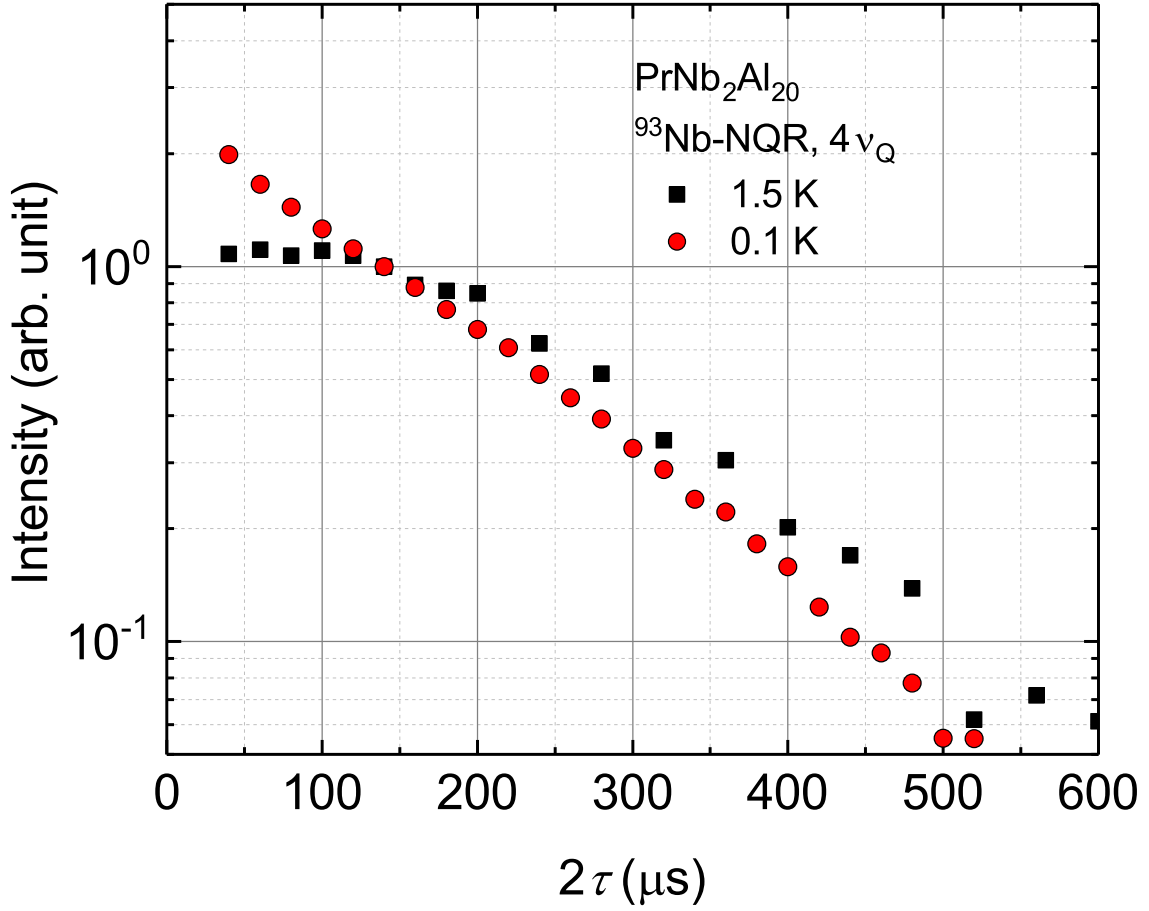


Figure 4.13: Temperature dependence of the ^{93}Nb -NQR spin-echo decay curve measured at the $4\nu_Q$ line and at 1.5 K and 0.1 K. Intensities are normalized by that at $2\tau = 140 \mu\text{s}$.

Figure 4.13 shows typical spin-echo decay curves measured at 1.5 K and 0.1 K. Here the spin-echo decay curve was obtained by recording the spin-echo amplitude $M(2\tau)$ of the ^{93}Nb - $4\nu_Q$ line as a function of the time interval τ between the first exciting and second refocusing pulses.

5 Discussion on $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

5.1 Analysis of the bulk magnetization in $\text{PrNb}_2\text{Al}_{20}$

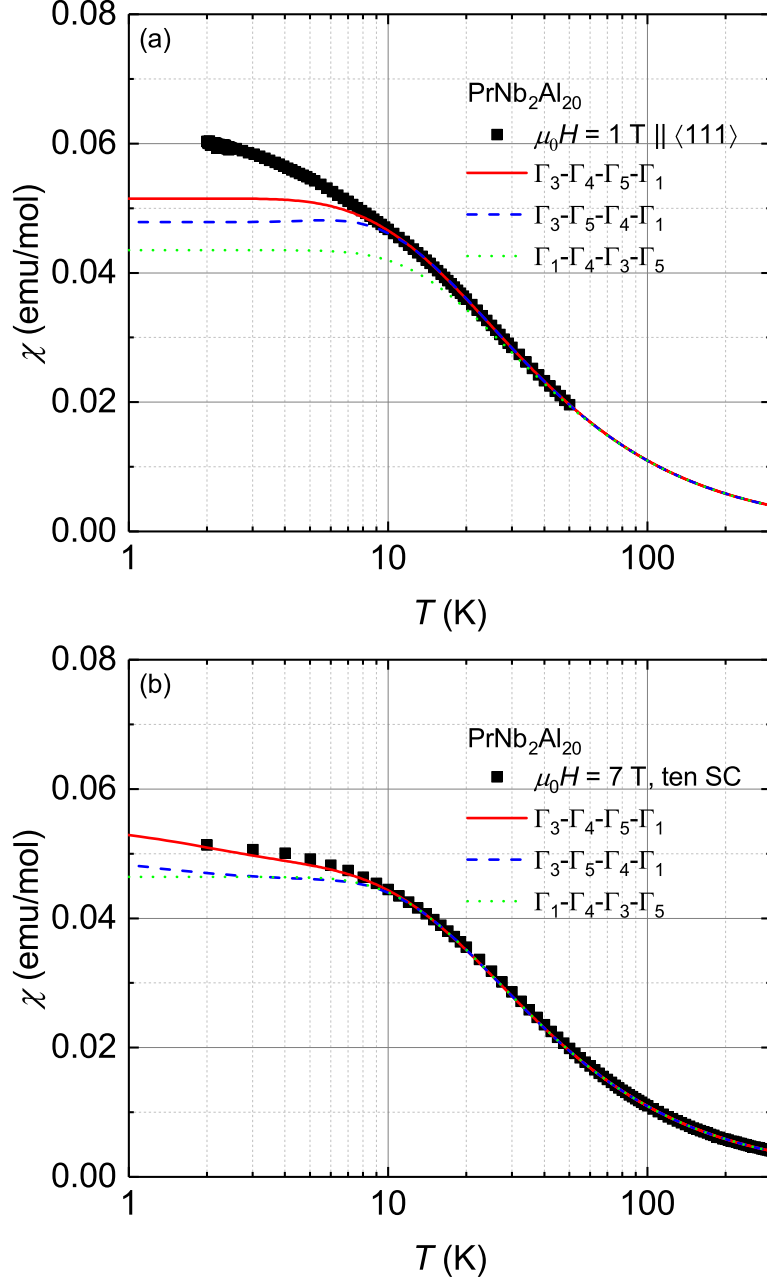


Figure 5.1: Temperature dependences of the magnetic susceptibility χ (a) at 1 T for a single crystal with $H \parallel \langle 111 \rangle$ and (b) at 7 T for randomly oriented single-crystal samples of $\text{PrT}_2\text{Al}_{20}$. χ at 7 T is cited from Ref. [11]. The red solid, blue dashed, and green dotted lines represent the calculated susceptibilities based on the CEF model described in the text.

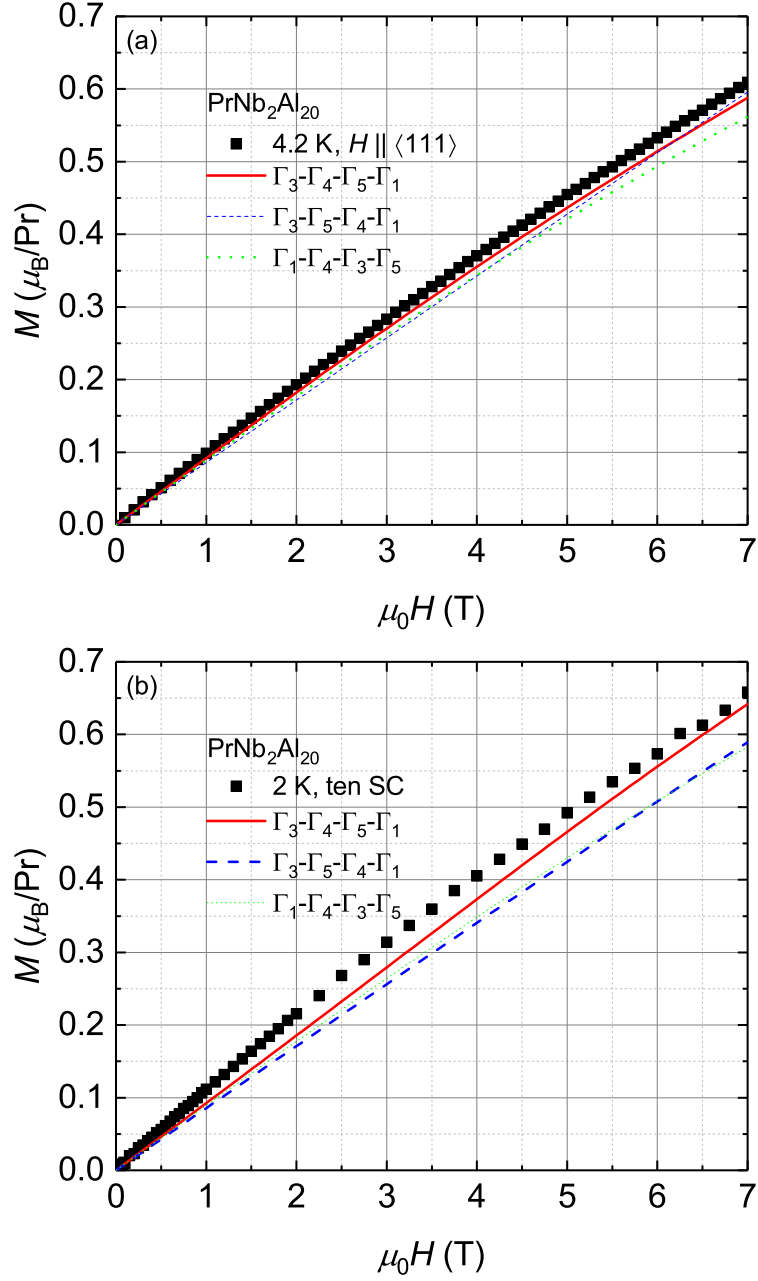


Figure 5.2: Field dependences of magnetization M (a) at 4.2 K for a single crystal with $H \parallel \langle 111 \rangle$ and (b) at 2 K for randomly oriented single-crystal samples. M at 2 K is cited from Ref. [11]. The red solid, blue dashed, and green dotted lines represent the calculated magnetizations based on the CEF model described in the text.

Figure 5.1(a) shows the magnetic susceptibility for a single-crystal sample measured at 1 T, $\chi(1 \text{ T})$, for $H \parallel \langle 111 \rangle$ below 50 K. Shown in Fig. 5.1(b) is the susceptibility $\chi(7 \text{ T})$, measured at 7 T cited from Ref. [11], where ten randomly oriented single-crystal samples were used.

At high temperatures of above 30 K, $\chi(1\text{ T})$ coincides with $\chi(7\text{ T})$. According to Ref. [11], the Curie-Weiss (CW) law fitting between 50 and 300 K yields μ_{eff} of $3.1\mu_{\text{B}}/\text{Pr}$ and Weiss temperature Θ_{W} of -11 K . In fact, the reduction of the effective moment is observed for the single-crystal sample and this may be an intrinsic property of $\text{PrNb}_2\text{Al}_{20}$. These findings imply that hybridization of the conduction electron and $4f$ electron state (c - f hybridization) is important. With decreasing temperature, both $\chi(1\text{ T})$ and $\chi(7\text{ T})$ increase gradually and $\chi(1\text{ T})$ begins to deviate from $\chi(7\text{ T})$ at around 30 K. At 2 K, $\chi(1\text{ T})$ is enhanced by 20% relative to $\chi(7\text{ T})$. However, no signature of a phase transition is detected down to 2 K. The behavior of χ at low temperatures is associated with the Van Vleck susceptibility for a small CEF-level splitting. Figures 5.2(a) and 5.2(b) show the magnetization M as a function of magnetic field. M increases linearly below $\approx 1\text{ T}$ and begins to deviate from the linear line.

In order to explain the results for the magnetic susceptibility and magnetization, we tentatively start from the localized $4f$ electron picture. When the single-ion Pr $4f^2$ CEF state is adopted for $\text{PrNb}_2\text{Al}_{20}$, the CEF Hamiltonian in T_d symmetry is given as $\mathcal{H} = B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4$, where B_m^l are the CEF parameters and O_m^l are the Stevens operators associated with multipole moments [45]. Then, the $J = 4$ manifold splits into a singlet $|\Gamma_1\rangle$, a doublet $|\Gamma_3\rangle$, and two triplets $|\Gamma_4\rangle$ and $|\Gamma_5\rangle$. The magnetic susceptibility and magnetization in the localized CEF model can be calculated by adding the Zeeman term to the CEF Hamiltonian as

$$\mathcal{H} = -g_J \mu_{\text{B}} \mathbf{J} \cdot (\mathbf{H} + \lambda \mathbf{M}) + W \left[\frac{x}{60} (O_4^0 + 5O_4^4) + \frac{1 - |x|}{1260} (O_6^0 - 21O_6^4) \right]. \quad (5.1)$$

The first term corresponds to the Zeeman interaction, where g_J is the Landé g -factor, $\mathbf{J}$ is the total angular momentum operator, H the applied field, λ the molecular field parameter corresponding to the Weiss temperature θ_{W} , and M the magnetization. The second term corresponds to the single-ion CEF Hamiltonian. W and x are the CEF parameters defined by Lea et al [46]. Note that the sign of W generally depends on the hybridization between the $4f$ electron state and ligand conduction electrons as well as the Coulomb potential of ligands. When we applied a magnetic field in the (θ, ϕ) direction, where θ and ϕ are the polar and azimuth angles with respect to the $[001]$ direction, the CEF susceptibility for the Pr ion is written as

$$\chi_{\text{CEF}} = \frac{N_{\text{A}} g_J \mu_{\text{B}}}{H} \frac{\sum_i \langle \Gamma_i | \mathbf{J} \cdot \mathbf{n} | \Gamma_i \rangle \exp(-E_{\Gamma_i}/k_{\text{B}}T)}{\sum_i \exp(-E_{\Gamma_i}/k_{\text{B}}T)}, \quad (5.2)$$

where $\mathbf{n} \equiv (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$, k_{B} is the Boltzmann constant, and E_{Γ_i} is the eigenvalue for eigenstate $|\Gamma_i\rangle$ ($i = 1, 3, 4, 5$) of the CEF state in the T_d symmetry.

First, the susceptibility data were fitted for temperatures of above 10 K by using the least-squares method to obtain the most probable values of W and x , where the molecular field parameter and the effective moment were set to $\lambda = -9.0$ mol/emu (corresponding to $\theta_W = -11$ K) and $\mu_{\text{eff}} = 3.1\mu_B$ as obtained by the CW fitting in order to avoid the proliferation of fitting parameters. In addition, the case of the magnetic ground state of Γ_4 or Γ_5 was assumed to be excluded from the present simulation. The values of W and x were varied independently by steps of 0.01 within the ranges of $-4 \leq W \leq 4$ and $-1 \leq x \leq 1$. The best-fit parameters to reproduce the susceptibility were obtained as $W = -0.73$ K and $x = 0.44$ and the CEF level scheme is Γ_3 (0 K)– Γ_4 (21.32 K)– Γ_5 (43.98 K)– Γ_1 (51.16 K). The best-fit curve is shown by the red solid line in Fig. 5.1. We also found that the parameter sets of $W = -0.90$ K and $x = -0.50$ [Γ_3 (0 K)– Γ_5 (24.30 K)– Γ_4 (31.50 K)– Γ_1 (75.60 K)] and $W = 1.37$ K and $x = -0.92$ [Γ_1 (0 K)– Γ_4 (26.85 K)– Γ_3 (46.03 K)– Γ_5 (74.64 K)] can reproduce the susceptibility data with a comparable residual sum of squares. The respective curves are shown by the blue dashed line and green dotted line in Fig. 5.1. In the calculation above, we did not treat the molecular field parameter self-consistently. In later calculations, we use the CEF parameters $W = -2.87$ K and $x = -0.60$ obtained from the IND measurement presented in §2.2.2.

These three CEF schemes can qualitatively reproduce the broad shoulder anomaly of C_{4f}/T around 20 K [11]. However, the peak position of C is at around 10 K, which is smaller than the experimental one. In order to determine which parameter set is better, we tried to fit the magnetization data. As clearly shown by the green dotted line in Fig. 5.1, we found that the calculated curve for the Γ_1 ground state provides worse fitting than those of the Γ_3 ground states. Thus, the present CEF analyses strongly indicate that the ground state is the Γ_3 doublet and the first excited state is either the Γ_4 or Γ_5 triplet. In fact, the logarithmic behavior of C_{4f}/T at low temperatures is evidence of CEF degrees of freedom at low energies and excludes the possibility of the Γ_1 CEF ground state [11].

5.2 Analysis of NMR/NQR spectra in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

In this section, we discuss the NMR/NQR spectrum analysis in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$), which is essential to perform the NMR/NQR measurements site-selectively.

5.2.1 ^{93}Nb -NMR/NQR in $\text{PrNb}_2\text{Al}_{20}$ powder

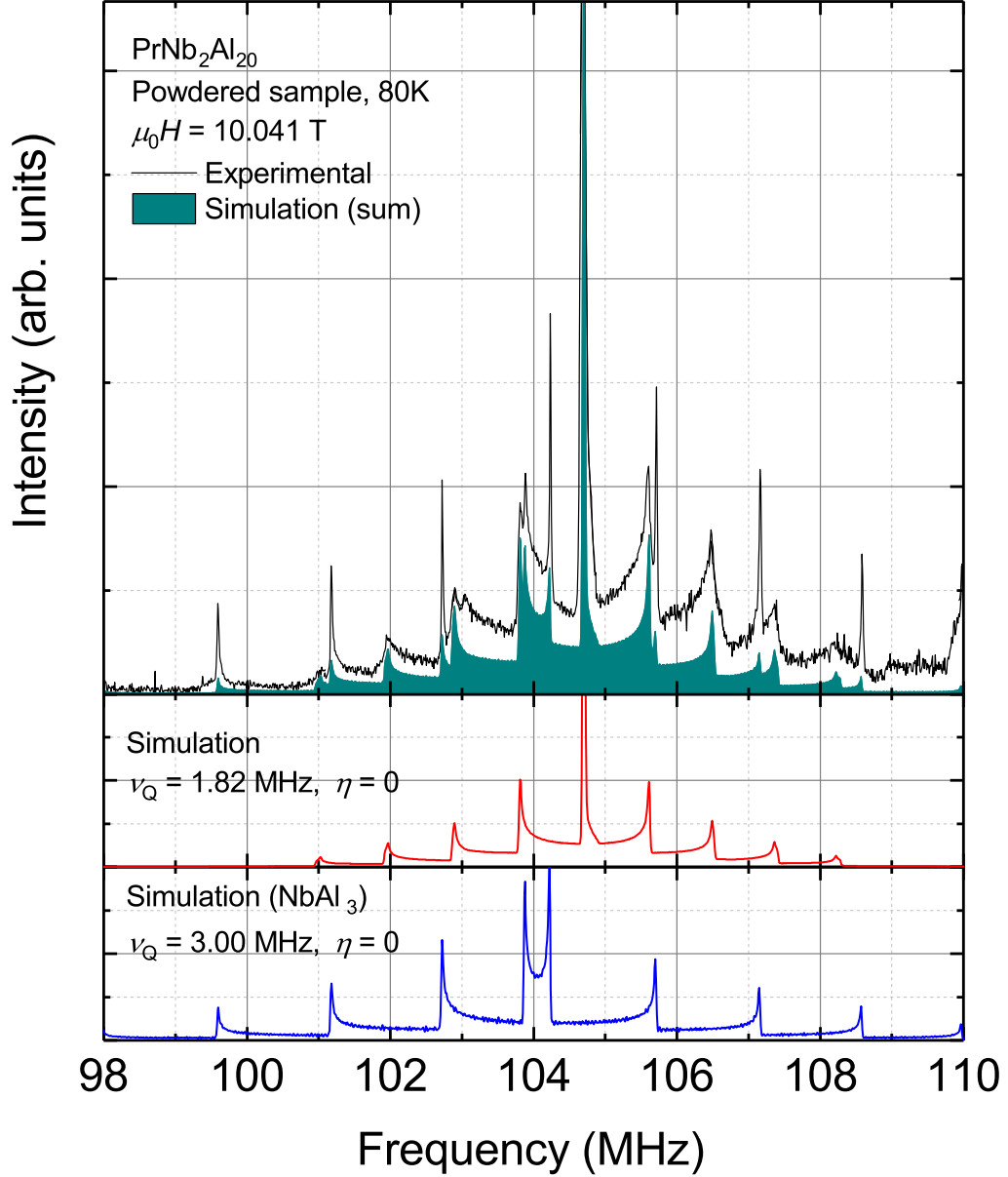


Figure 5.3: Nb-NMR spectrum obtained at $\mu_0 H = 10.041$ T, 80 K. The red and blue solid lines are the calculated lines for powder $\text{PrNb}_2\text{Al}_{20}$ and NbAl_3 , respectively. Dark cyan line is the sum of two simulations. Details are described in the text.

Figure 5.3 shows the frequency-swept ^{93}Nb -NMR spectrum obtained at $\mu_0 H = 10.041\text{ T}$ and $T = 80\text{ K}$. In order to reproduce the observed line profile, resonance frequencies were calculated for a powder sample by an exact-diagonalization method for the $(2I + 1) \times (2I + 1)$ nuclear spin Hamiltonian matrix of ^{93}Nb nucleus. The Hamiltonian can be written as described in §3, in which Eqs.(3.5–3.8) can be rewritten as

$$\mathcal{H}_{\text{hf}} = -\gamma_n \hbar \mathbf{I} \cdot (\tilde{\mathbf{D}} + \tilde{\mathbf{K}}) \cdot \mathbf{H}_0. \quad (5.3)$$

$\tilde{\mathbf{K}}$ describes the hyperfine field due to the c - f hybridization and $\tilde{\mathbf{D}}$ is the classical dipole field created by $4f$ electrons. In the analysis for the powder sample, we ignore the effect of $\tilde{\mathbf{D}}$ for simplicity. For a Nb case, the Nb site is of threefold symmetry in $\text{PrNb}_2\text{Al}_{20}$, then the $\tilde{\mathbf{K}}$ and EFG hold axial symmetry and their maximum principal axes direct one of the $\langle 111 \rangle$ directions. Then, η is zero and $\tilde{\mathbf{K}}$ is characterized by the isotropic part $K_{\text{iso}} \equiv (K_{11} + K_{22} + K_{33})/3$ and axial part $K_{\text{axi}} = [K_{33} - (K_{11} + K_{22})/2]/3$, where K_{ii} 's are the principal values of $\tilde{\mathbf{K}}$.

The red solid line in Fig. 5.3 is the result of the simulation for the powder sample, where the principal axes of the EFG and the Knight shift are assumed to randomly distribute against the applied magnetic field. From the simulation, ν_Q , K_{iso} , and K_{axi} is extracted to be $\nu_Q = 1.82\text{ MHz}$, $K_{\text{iso}} = 0.25\text{ ‰}$, and $K_{\text{axi}} = 0.15\text{ ‰}$, respectively. Note that very sharp NMR signals were observed. The sharp signals are found to be attributed to the ^{93}Nb signals from the NbAl_3 impurity [47]. With ^{93}Nb -NQR parameters ($\nu_Q = 2.9\text{ MHz}$) of NbAl_3 reported by Lue *et al.* [48], the sharp NMR signals are well reproduced as indicated by blue lines in Fig. 5.3.

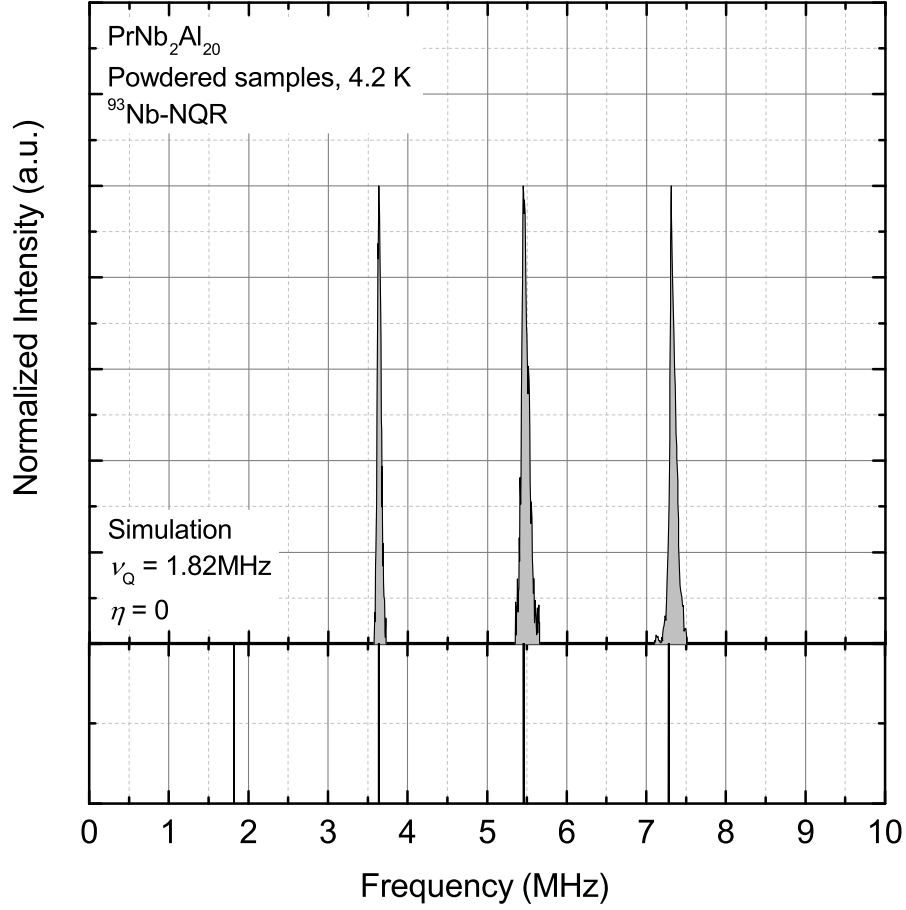


Figure 5.4: (Upper) ^{93}Nb -NQR spectrum obtained at 4.2 K. (Lower) Calculated NQR frequency by using NQR parameters obtained from the NMR measurement.

To confirm the validity of the obtained ν_Q , ^{93}Nb -NQR experiment was performed. Shown in Fig. 5.4 is the obtained ^{93}Nb -NQR spectrum at 4.2 K. The NQR lines shown in the upper part are observed at equal intervals, which can be reproduced by using the NQR parameters ($\nu_Q = 1.82$ MHz and $\eta = 0$) obtained from the ^{93}Nb -NMR as shown in the lower part of the figure. Then, the lines are assigned as the ^{93}Nb -NQR resonances for ($m = \pm 3/2 \rightleftharpoons \pm 5/2$), ($m = \pm 5/2 \rightleftharpoons \pm 7/2$), and ($m = \pm 7/2 \rightleftharpoons \pm 9/2$) transitions, where the ($m = \pm 1/2 \rightleftharpoons \pm 3/2$) transition cannot be observed because of the experimental setup. The NQR signals for the NbAl_3 -impurity were also observed at 3, 6, 9, and 12 MHz.

5.2.2 ^{27}Al -NMR/NQR in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$) powder

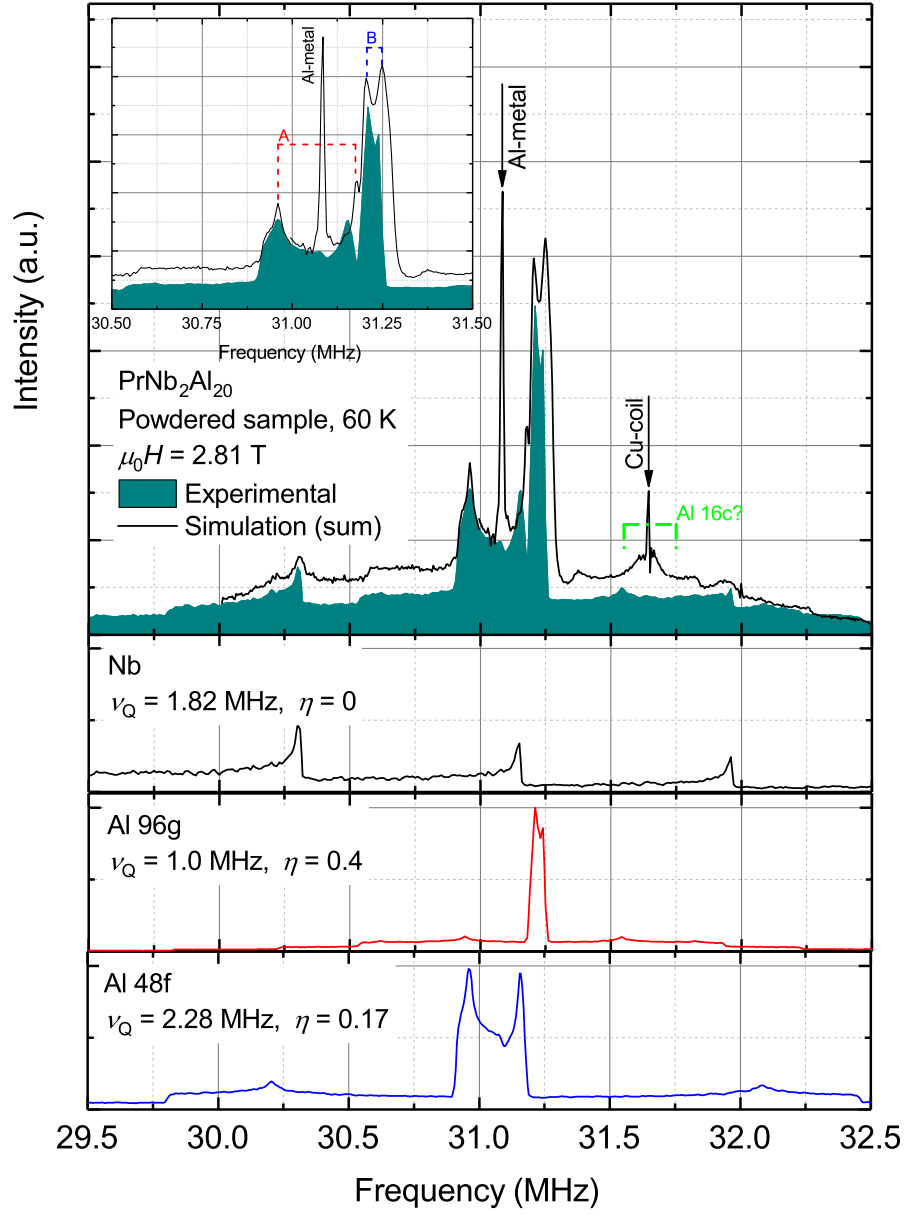


Figure 5.5: ^{27}Al -NMR spectrum obtained at $\mu_0 H = 2.81$ T, 60 K. The thick black, red, and blue lines are the calculated lines for powder samples of $\text{PrNb}_2\text{Al}_{20}$. Dark cyan area is the sum of two simulations. Details are described in the text. Inset: the enlarged line profile at around Al central transitions. Sharp lines from the impurity Al-metal and Cu-coil are indicated by black arrows.

Figure 5.5 shows the frequency-swept ^{93}Nb - and ^{27}Al -NMR line obtained at $\mu_0 H = 2.81$ T and 60 K. The black solid line in the second figure from the top of Fig. 5.5 is the result of the

simulation described in §5.2.1 using $\nu_Q = 1.82$ MHz and $\eta = 0$. In addition to the signals from ^{93}Nb , several sharp peaks were observed as shown in the inset of Fig. 5.5. The sharp peak at 31.08 MHz comes from the impurity Al-metal from the residual flux. The central line of the NMR powder pattern spectrum (corresponding to $(-1/2 \rightleftharpoons +1/2)$ transition) can be split by the second order perturbation of the nuclear quadrupole interaction. Here, we assumed that peaks around 30.96 and 31.18 MHz originate from one Al site (line A) and peaks around 31.21 and 31.25 MHz (line B) originate from another Al site. The separation of two peaks for the lines A and B are estimated to be $\Delta\nu_A \approx 0.22$ MHz and $\Delta\nu_B \approx 0.04$ MHz, respectively. Theoretically, the central line should have the typical line shape owing to the second order quadrupole perturbation. In this case, the width of the separation of the central line is approximately expressed as

$$\Delta\nu = \frac{25\nu_Q^2[I(I+1) - 3/4]}{144\nu_0} \quad (5.4)$$

where $\nu_0 = {}^{27}\gamma_n H = 31.17$ MHz is the Zeeman frequency in the absence of nuclear quadrupole interaction [49, 50]. In this formula, the EFG is assumed to be axial ($\eta = 0$) and the effect of the anisotropic Knight shift is ignored. By using Eq. (5.4) and $\Delta\nu$'s, we extracted ν_Q as $\nu_Q^A \approx 1.1$ MHz (line A) and $\nu_Q^B \approx 2.5$ MHz (line B). As discussed in the next paragraph, the obtained ν_Q 's have a good agreement with the result of other $\text{PrT}_2\text{Al}_{20}$ compounds.

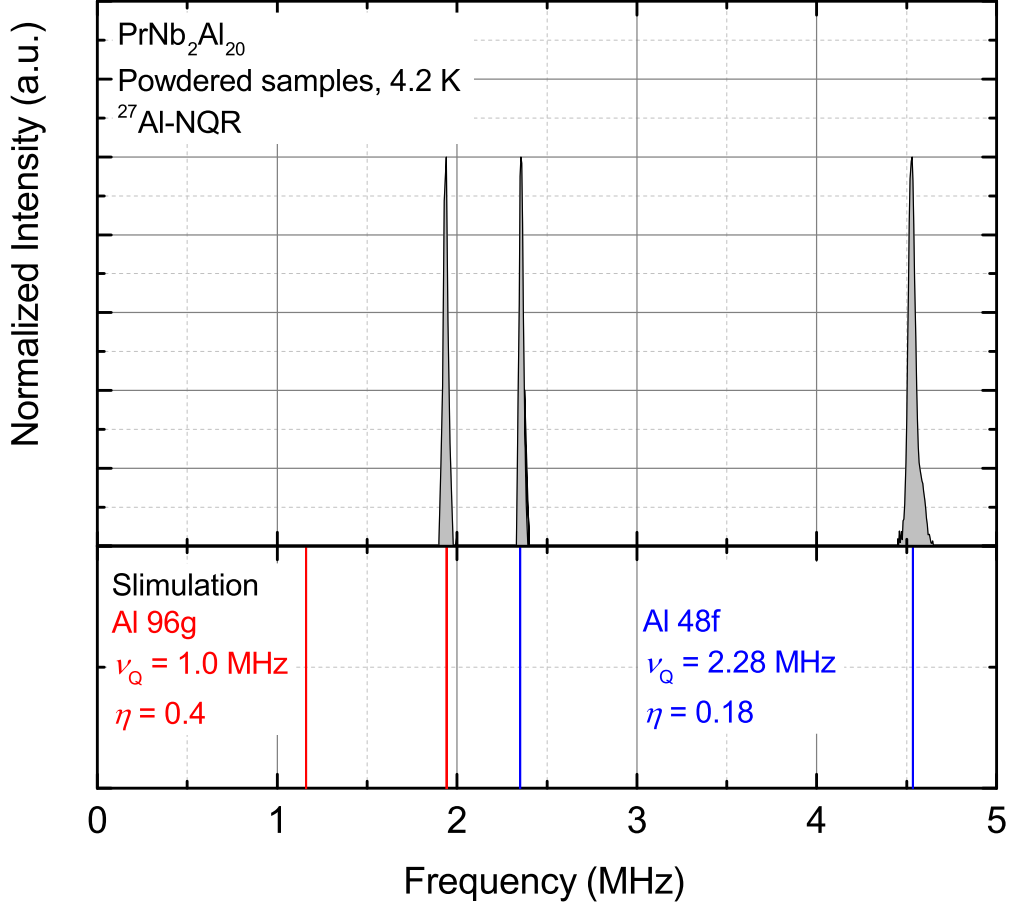


Figure 5.6: (Upper) ^{93}Nb -NQR spectrum obtained at 4.2 K. (Lower) Calculated NQR frequency by using NQR parameters obtained from the NMR measurement.

The upper panel of Fig. 5.6 shows ^{27}Al -NQR lines obtained at 4.2 K. We observed sharp NQR lines at around 1.94, 2.36, and 4.55 MHz. We calculated NQR resonance frequencies by using the estimated ν_Q 's and the nuclear quadrupole Hamiltonian as described in the previous section. The result is shown by the red and blue lines in the lower panel of Fig. 5.6. ν_Q and η are obtained by fitting these observed NQR lines. The obtained ν_Q and η for site A are $\nu_Q = 2.28 \text{ MHz}$ and $\eta = 0.17$. For site B, $\nu_Q = 1.0 \text{ MHz}$ and $\eta = 0.4$ are obtained. The red and blue solid lines in the third and fourth from the top of Fig. 5.5 are the results of the calculation using these NQR parameters. The dark cyan area in the top of Fig. 5.5 shows the sum of calculated one Nb and two Al lines, which well reproduces the experimental result. Then, the obtained NQR parameters seem to be reasonable ones. Tokunaga *et al.* reported ^{27}Al -NQR parameters for $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V}$) from the single crystal NMR measurements. They analyzed ^{27}Al -NMR spectrum and extracted NQR parameters to be $\nu_Q \approx 1.9\text{--}2 \text{ MHz}$ and $\eta \approx 0.145$ for Al 48f site and $\nu_Q \approx 0.8\text{--}0.9 \text{ MHz}$ and $\eta \approx 0.3\text{--}0.4$ for Al 96g site. Thus,

we concluded that the site A corresponds to Al 48*f* site and B corresponds to Al 96*g* site. However, the lines around 31.7 MHz could not be reproduced by the above calculation. We speculate that this signal originates from Al 16*c* site because of its small fraction.

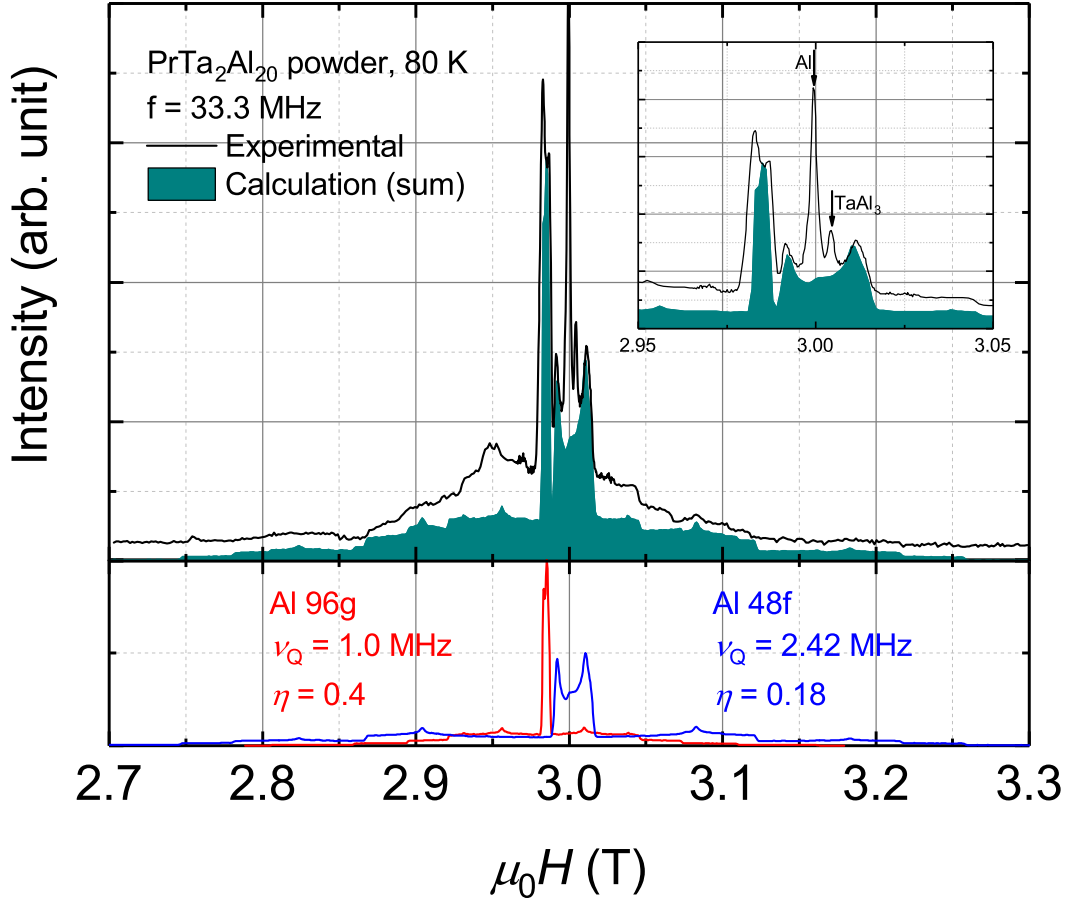


Figure 5.7: (Upper) ^{27}Al -NMR spectrum obtained at around $\mu_0 H = 3$ T, 80 K. Inset shows the enlarged view of the central transition. (Lower) Calculated NMR lines for Al 48*f* and Al 96*g* sites. The dark cyan area in the upper figure is the sum of these two simulations. Signals from the impurity Al-metal and TaAl_3 are indicated by black arrows.

The black solid line in Fig. 5.7 shows the field-swept ^{27}Al -NMR spectrum for powder sample of $\text{PrTa}_2\text{Al}_{20}$ obtained at the fixed frequency of 33.3 MHz and at 80 K. The obtained NMR spectrum consists of the sharp peaks as discussed for $\text{PrNb}_2\text{Al}_{20}$. Sharp lines marked by the black arrows in the inset of Fig. 5.7 comes from the impurities of Al-metal and TaAl_3 . The estimation of ν_Q by using Eq. 5.4 gives $\nu_Q \approx 1.1$ MHz for the peaks at 2.983 and 2.987 T and ≈ 2.3 MHz for the peaks at 2.992 and 3.011 T.

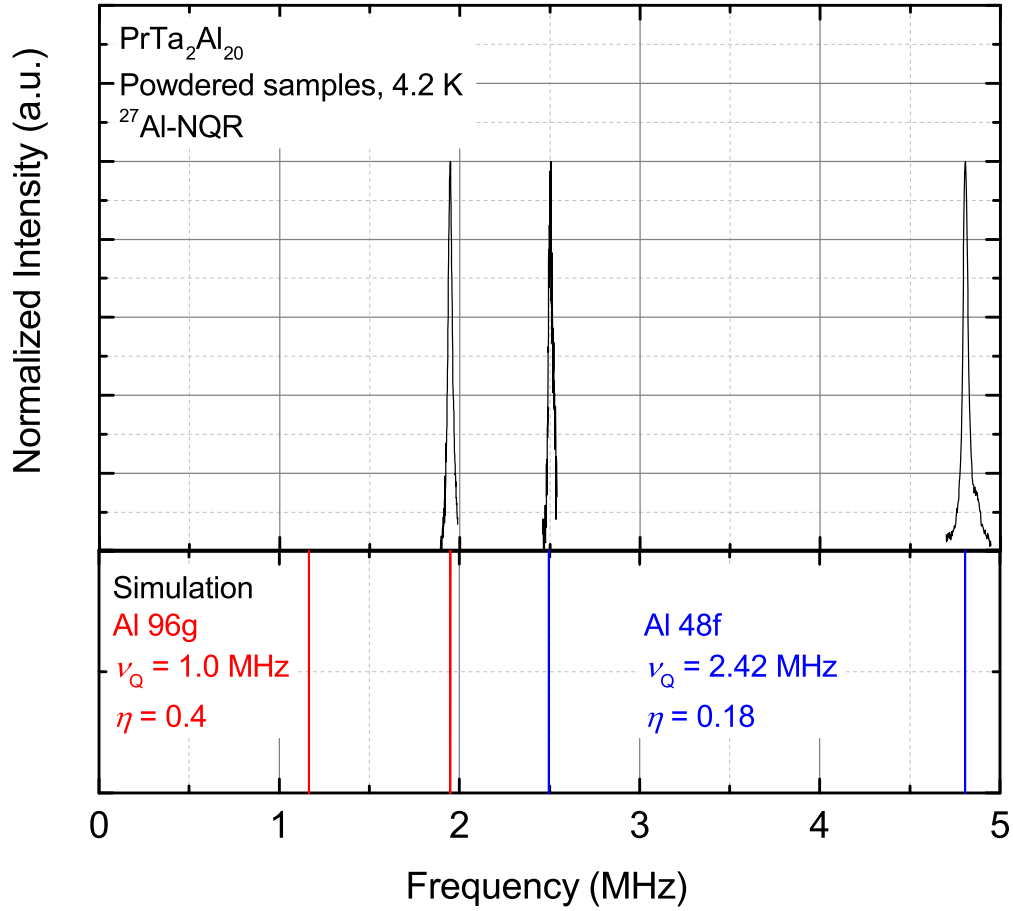


Figure 5.8: (Upper) ^{27}Al -NQR spectrum obtained at 4.2 K. (Lower) Calculated NQR lines for Al 48*f* and Al 96*g* sites.

Figure 5.8 shows the NQR lines obtained at 4.2 K. Sharp three lines are observed at around 1.95, 2.50, and 4.81 MHz. By using the results of other $\text{PrT}_2\text{Al}_{20}$ systems, ν_Q and η are determined to be $\nu_Q = 2.42$ MHz and $\eta = 0.18$ for Al 48*f* site, and $\nu_Q = 1.0$ MHz and $\eta = 0.4$ for Al 96*g* site. The dark cyan, red blue lines in Fig. 5.7 is the result of the simulation by using these NQR parameters. The agreement between experiment and simulation is satisfactory, then the validity of the obtained NQR parameters are confirmed.

$T = \text{Nb}$	ν_Q (MHz)	η	$T = \text{Ta}$	ν_Q (MHz)	η
Nb	1.82	0			
Al 48 <i>f</i>	2.28	0.17	Al 48 <i>f</i>	2.42	0.18
Al 96 <i>g</i>	1.0	0.4	Al 96 <i>g</i>	1.0	0.4

Table 5.1: The obtained ^{27}Al -NQR parameters of $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb}$ and Ta).

The obtained NQR parameters are summarized in Table 5.1.

5.2.3 Analysis of NMR spectra of $\text{PrNb}_2\text{Al}_{20}$ single crystal

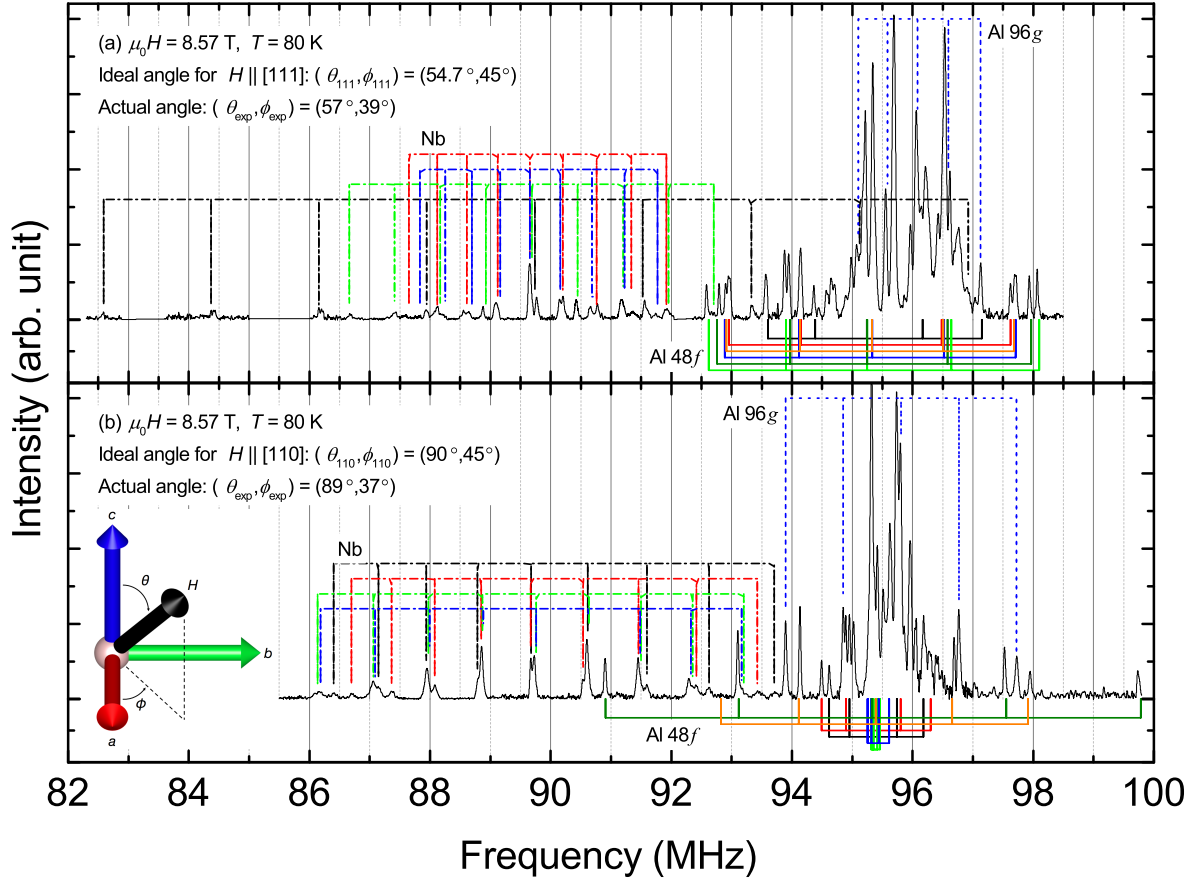


Figure 5.9: NMR spectrum obtained for single crystal $\text{PrNb}_2\text{Al}_{20}$ with (a) $H \parallel \langle 111 \rangle$ and (b) $H \parallel \langle 110 \rangle$. For both cases, the ideal angles and the actual angles obtained from the fitting are given by $(\theta_{111/110}, \phi_{111/110})$ and $(\theta_{\text{exp}}, \phi_{\text{exp}})$, respectively. Colored dash-dotted, solid and dashed lines are the calculated resonance frequencies for Nb, Al 48f, and Al 96g sites, respectively. Inset of (b): Definition of the field angle with respect to the crystal axis directions.

Figure 5.9 shows ^{93}Nb - and ^{27}Al -NMR spectra in a single crystal $\text{PrNb}_2\text{Al}_{20}$ obtained at the fixed magnetic field 8.57 T applied parallel to one of the (a) $\langle 111 \rangle$ and (b) $\langle 110 \rangle$ axes, and at a temperature of 80 K. Each of the resonance lines are as sharp as about 30 kHz. Due to the local symmetry at the ligand sites which is lower than cubic, as described below, these sites split further under the magnetic field. In order to deconvolute the obtained lines into the above sites, we carried out the simulation numerically solving the $(2I+1) \times (2I+1)$ nuclear spin Hamiltonian $\mathcal{H}$ by an exact diagonalization method. Such a Hamiltonian can be written as discussed in §5.2.1. In this analysis, we treat $\tilde{K}$ and $\tilde{D}$ separately. $\tilde{K}$ is decomposed into the isotropic part K_{iso} and the anisotropic part $\tilde{K}_{\text{ani}}$. $\tilde{K}_{\text{ani}}$ and $\tilde{D}$ are traceless and designated by their principal

values (K_{11}, K_{22}, K_{33}) and (D_{11}, D_{22}, D_{33}) that satisfy the relation of $|K_{33}| \geq |K_{22}| \geq |K_{11}|$ and $|D_{33}| \geq |D_{22}| \geq |D_{11}|$.

In order to calculate NMR lines, we have to know the principal values and principal axis directions of $\tilde{V}$, $\tilde{D}$, and $\tilde{K}$. The principal values of $\tilde{D}$ are calculated by the lattice sum of the classical dipole field $\mathbf{H}_D = \sum_i \left[-\boldsymbol{\mu}_i/r_i^3 + (\boldsymbol{\mu}_i \cdot \mathbf{r}_i)\mathbf{r}_i/r_i^5 \right]$, where $\boldsymbol{\mu}_i = g_J \mu_B \mathbf{J}_i$ is the 4f electronic magnetic dipole in which g_J , μ_B , and $\mathbf{r}_i$ are the Landé g-factor, the Bohr magneton, and the distance between the site considered and i th Pr site, respectively. The magnitude of magnetic dipole is estimated to be $\approx 0.2 \mu_B$ at 80 K from the magnetization analysis [11, 51]. ν_Q and η for Nb, Al 48f, and Al 96g sites are already determined in the previous section [42, 47, 52]. The principal values of $\tilde{K}$ are treated as fitting parameters.

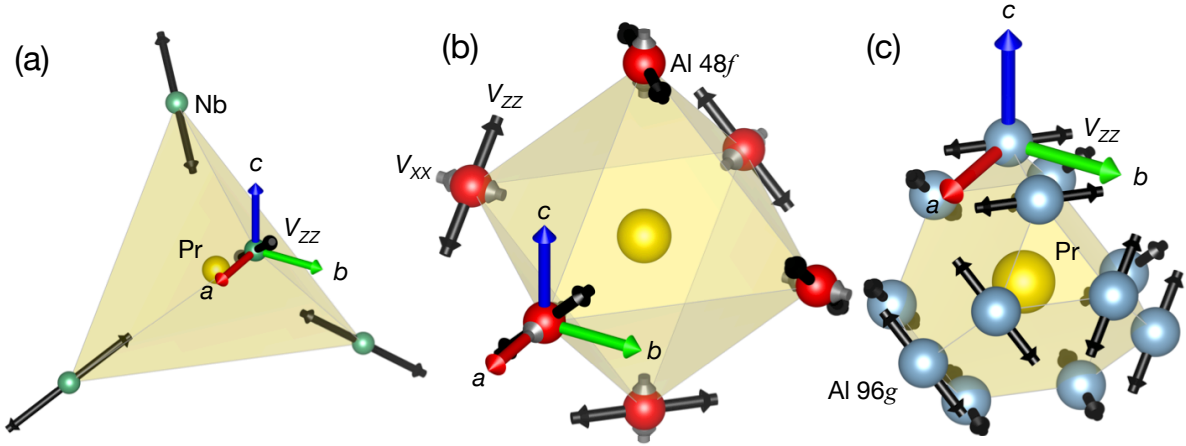


Figure 5.10: (a) Pr and surrounding Nb atoms with crystal axes and local symmetry axis at Nb sites. Red, light green, and blue arrows denote crystal a , b , and c axes, respectively. Black arrows indicate local threefold rotation axes, which coincide with the maximum principal axis directions of $\tilde{V}$, $\tilde{K}$, and $\tilde{D}$ in this case. (b) Pr and nearest-neighboring Al 48f atoms with the crystal and EFG principal axes. Black and gray arrows indicate the maximum (V_{ZZ}) and minimum (V_{XX}) principal axis directions of the EFG tensor from the band calculation, respectively. (c) Pr and nearest-neighboring Al 96g atoms with the crystal and EFG principal axes. Black arrows indicate V_{ZZ} directions from the band calculation.

Next, we consider the principal axis directions. Generally, these directions do not coincide with the crystal axes or with each other due to the local symmetry at the ligand sites. In such a case, the analysis taking into account of the local symmetry is previously reported [52, 53, 54, 55, 56, 57]. Shown in Fig. 5.10 is the geometry of neighboring Nb, Al 48f, and Al 96g atoms around a Pr atom. Crystal axis directions at these ligand sites are also represented. For the Nb site with local symmetry of $\bar{3}m$, the maximum principal axis direction coincides with the local threefold rotation axis. As shown in Fig. 5.10(a) with the crystal axis directions,

this axis is parallel to $[111]$ direction for the Nb site at $(1/2, 1/2, 1/2)$. $\tilde{V}$, $\tilde{D}$, and $\tilde{K}$ are axially symmetric around this axis. The Al 16c site has the local symmetry of $\bar{3}m$, thus the principal axis directions are the same with those for the Nb site. For the Al 48f site at which local symmetry is $2.mm$, there are two mirror planes. For example, the Al 48f site at $(1/8, 1/8, z)$ has mirror planes (110) and $(1\bar{1}0)$. In this case, the principal axis directions are constrained in these mirror planes but the maximum principal axis direction cannot be determined beforehand. For the Al 96g site at which the local symmetry is $.m$, there are only one mirror plane which is parallel to one of the $\{110\}$ plane. The Al 96g site at (x, x, z) has $(1\bar{1}0)$ mirror plane. In this case, one of the three principal axes are perpendicular to the plane and the other two axes are in the plane. Since the principal axis directions in the plane cannot be predetermined, $\tilde{V}$ is calculated for each sites by a band calculation in local density approximation for the isostructural $\text{LaNb}_2\text{Al}_{20}$ [52]. The details of the calculation method are described in Ref. [58]. As shown in Fig. 5.10(b) with the crystal axis directions, V_{ZZ} and V_{XX} directions for the Al 48f site at $(x, 1/8, 1/8)$ are obtained to be $[011]$ and $[100]$ directions, respectively. Figure 5.10(c) shows the crystal axis and V_{ZZ} directions for the Al 96g site. For the Al 96g site at (x, x, z) , the V_{ZZ} direction is calculated to be parallel to the $[1\bar{1}0]$ direction.

Using the principal values and principal axis directions, we can obtain each of the tensor components in the crystal coordinate by an appropriate frame transformation $\tilde{T}_c = R\tilde{T}_pR^{-1}$, where $\tilde{T}_p$ and $\tilde{T}_c$ are the representations of a tensor in its principal and crystal coordinate, respectively, and R is a frame transformation matrix between these coordinates. In addition, tensor components are transformed from one site to another under symmetry operations such as 120° rotation around one of the $\langle 111 \rangle$ axes and mirror operation for one of the $\{110\}$ planes.

$H \parallel \langle 111 \rangle$	NMR sites	NMR lines	$H \parallel \langle 110 \rangle$	NMR sites	NMR lines
Nb	2	18	Nb	2	18
Al 16c	2	10	Al 16c	2	10
Al 48f	2	10	Al 48f	3	15
Al 96g	3	15	Al 96g	4	20

Table 5.2: (Left) The number of NMR sites and corresponding number of NMR lines for $H \parallel \langle 111 \rangle$ case. (Right) The number of NMR sites and corresponding number of NMR lines for $H \parallel \langle 110 \rangle$ case.

Based on the above considerations, we analyzed the observed NMR lines. In Table 5.2, we summarized the number of the NMR sites and corresponding number of NMR lines for two magnetic field directions. As shown in Fig. 5.9, the number of the observed NMR lines are larger than expected number of NMR lines for each of the field directions. This is due to a misalignment of the sample, which causes further splitting of the NMR sites. Such a

	ν_Q (MHz) / η (exp.)	ν_Q (MHz) / η (cal.)	V_{ZZ} (cal.)
Nb	1.82 / 0	1.238 / 0	$\parallel \langle 111 \rangle$
Al 16c	– / –	0.715 / 0	$\parallel \langle 111 \rangle$
Al 48f	2.28 / 0.17	2.427 / 0.191	$\parallel \langle 110 \rangle$
Al 96g	0.98 / 0.46	1.005 / 0.348	$\parallel \langle 110 \rangle$

	(D_1, D_2, D_3) (%) (calc.)	D_3	(K_{iso}, K_1, K_2, K_3) (%) (exp.)	K_3
Nb	(0.018, 0.018, -0.036)	$\parallel \langle 111 \rangle$	(0.43, -0.08, -0.08, 0.16)	$\parallel \langle 111 \rangle$
Al 16c	(-0.132, -0.132, 0.264)	$\parallel \langle 111 \rangle$	–	–
Al 48f	(0.005, 0.025, -0.030)	$\parallel \langle 110 \rangle$	(0.25, 0.03, -0.09, 0.12)	$\parallel \langle 1\bar{1}0 \rangle$
Al 96g	(-0.026, -0.081, 0.107)	$\perp \langle 110 \rangle$	–	–

Table 5.3: (Upper) The experimental and calculated NQR parameters for each of the ligand sites. (Lower) The calculated dipole field tensor and experimentally determined Knight shift tensor with D_3 and K_3 directions, respectively. The magnitude of D_i 's and K_i 's is given as the relative values for the Zeeman frequency $\gamma_n H / 2\pi$. As described in the text, NMR signals from the Al 16c site cannot be deconvoluted due to the overlapping of NMR lines.

misalignment is inevitable since we use a uniaxial goniometer in the present measurement. For general field direction, we have four Nb, six Al 48f, and twelve Al 96g sites.

First, we determined the exact field angle by calculating the ^{93}Nb -NMR lines because the principal axis directions of $\tilde{V}$, $\tilde{D}$, and $\tilde{K}$ at Nb sites are uniquely determined as discussed above. We defined the field angle θ to be the polar angle of H from c -axis and ϕ to be the azimuthal angle of H in ab -plane as shown in the inset of Fig. 5.9. When we applied the magnetic field parallel to the $[111]$ direction, we have $(\theta_{111}, \phi_{111}) = (54.74^\circ, 45^\circ)$. Similarly, when we applied the magnetic field parallel to the $[110]$ direction, we have $(\theta_{110}, \phi_{110}) = (90^\circ, 45^\circ)$. As shown by the dash-dotted lines in Fig. 5.9, we could assigned ^{93}Nb -NMR lines to the four Nb sites. From the fitting of these lines, we obtained $(\theta_{\text{exp}}, \phi_{\text{exp}} = 57^\circ, 39^\circ)$ for Fig. 5.9(a) and $(\theta_{\text{exp}}, \phi_{\text{exp}} = 89^\circ, 37^\circ)$ for Fig. 5.9(b). Obtained NQR and Knight shift parameters are summarized in Table 5.3, which is consistent with the result of the band calculation. The calculated values are consistent with the values obtained above [42, 47, 52]. Therefore, we could determined the field angle for two magnetic field directions.

Next, we analyzed the ^{27}Al -NMR lines by using the obtained field angles. NMR lines from Al 16c and 96g sites overlap strongly each other so that, in general, it is difficult to deconvolute them. Nevertheless, we could assigned NMR lines from one of the Al 96g site since these lines could be clearly separated from another Al lines as shown by the dashed lines in Fig. 5.9. The obtained NQR parameters ($\nu_Q = 0.98$ MHz, $\eta = 0.46$) are consistent with the previous NMR and NQR result [52] and the V_{ZZ} direction corresponds to the predetermined one by

the band calculation. For more precise deconvolution of the Al 16*c* and 96*g* lines, the NMR measurement using a double-axis goniometer and the NQR measurement below 1.5 MHz are needed.

Finally, we discuss about the ^{27}Al -NMR lines from the Al 48*f* site. As shown by the solid lines in Fig. 5.9, all of the ^{27}Al -NMR lines from the Al 48*f* site are well reproduced by the simulation and the obtained NQR parameters ($\nu_Q = 2.28$ MHz, $\eta = 0.17$) are consistent with the previous reports [51, 52]. The EFG principal axis directions at the Al 48*f* site correspond to the calculated ones, thus the validity of the band calculation is confirmed. In addition, we could determine $\tilde{K}$ at the Al 48*f* site as shown in Table 5.3.

5.3 Static properties of $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

5.3.1 Determination of the CEF excited state in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

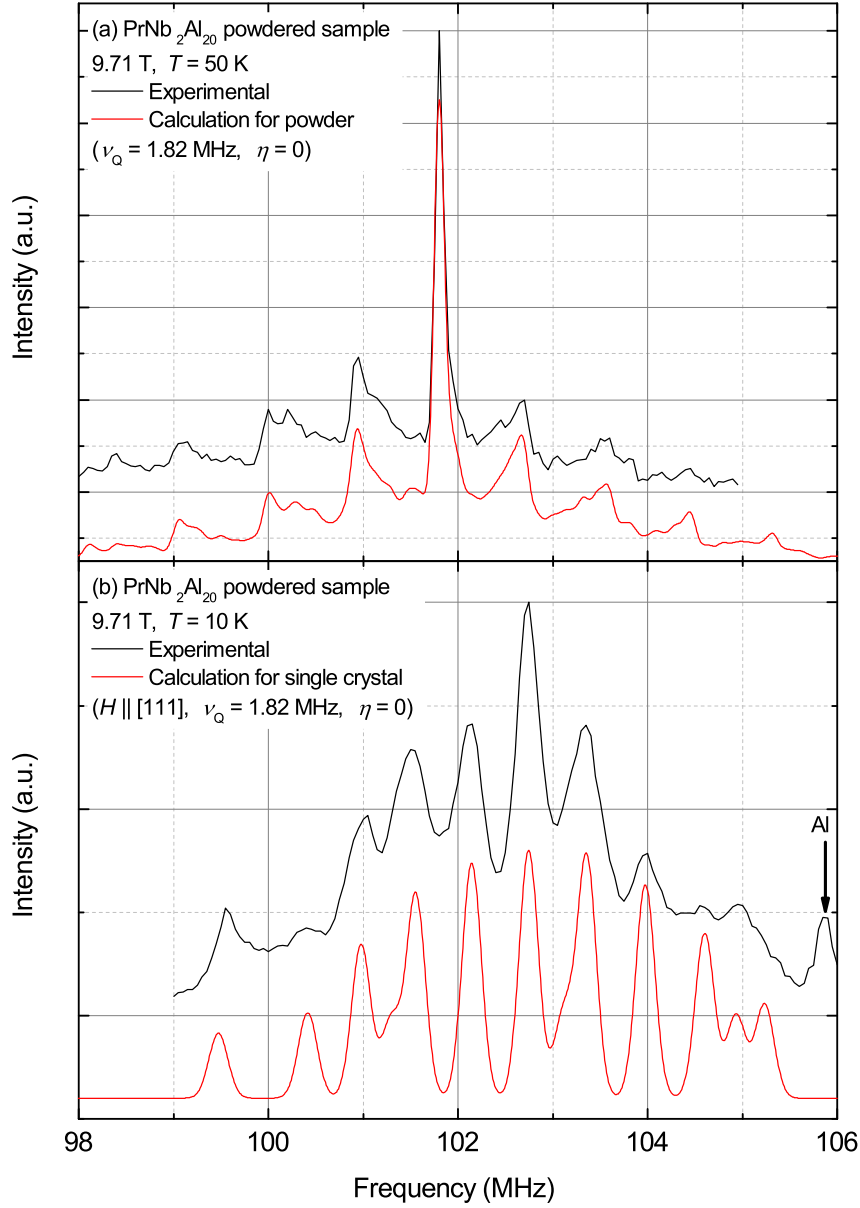


Figure 5.11: The temperature dependence of the ^{93}Nb -NMR spectrum obtained at 9.7 T. (a) The black solid line is obtained at 50 K and the red solid one is the calculation in which grains of the sample are assumed to be aligned randomly against the external field. (b) The black solid line is obtained at 10 K and the red solid one is the calculation in which grains of the sample are assumed to be aligned to one of the $\langle 111 \rangle$ directions parallel to the external field. The black arrow indicates the signal from the ^{27}Al -nuclei in $\text{PrNb}_2\text{Al}_{20}$.

First, we discuss the CEF scheme in $\text{PrNb}_2\text{Al}_{20}$ by analyzing the NMR lineshape. Figure 5.11 shows typical frequency-swept ^{93}Nb -NMR spectra obtained at a fixed magnetic field of 9.7 T. At high temperatures above 40 K, the observed NMR line profile exhibit a typical powder pattern, which is consistent with the above discussion [47]. At low temperatures, the line profile cannot be fitted by the powder pattern. As shown by the red solid line in Fig. 5.11(a), the line profile at 50 K is well reproduced by using the previously determined $^{93}\text{NMR/NQR}$ parameters [42, 47, 52] assuming that the grains of sample are randomly oriented in the external field. However, at 10 K, the line profile cannot be reproduced assuming that the sample has random orientation, but is rather reproduced by assuming that the grains are aligned parallel to one of the $\langle 111 \rangle$ directions which is parallel to the external field. As discussed below, this alignment of the sample can be explained by the magnetic anisotropy that originates from the CEF effect.

The random orientation of grains confirms that the magnetic anisotropy is weak at high temperatures as expected to the cubic structure. At lower temperatures, however, the alignment of grains indicates the development of the magnetic anisotropy in $\text{PrNb}_2\text{Al}_{20}$. In the f electron system which has the strong c - f hybridization, the method to separate the localized and itinerant nature of f electrons is not well established. Hence, we tentatively analyzes the magnetic anisotropy of $\text{PrNb}_2\text{Al}_{20}$ based on the simple CEF model, as used for the magnetization analysis described above. In the previous section §5.1, the analysis of χ and M shows that the CEF scheme of the ground Γ_3 doublet and the first excited magnetic triplet Γ_4 or Γ_5 well reproduces the experimental results [51]. As shown below, the difference of the first excited state (Γ_4 or Γ_5) gives a difference in the static magnetic response at low temperatures. In order to check the magnetic response due the CEF first excited state, we calculated the magnetic susceptibility in the framework of the localized CEF model by adding the Zeeman term as discussed in §5.1 [51].

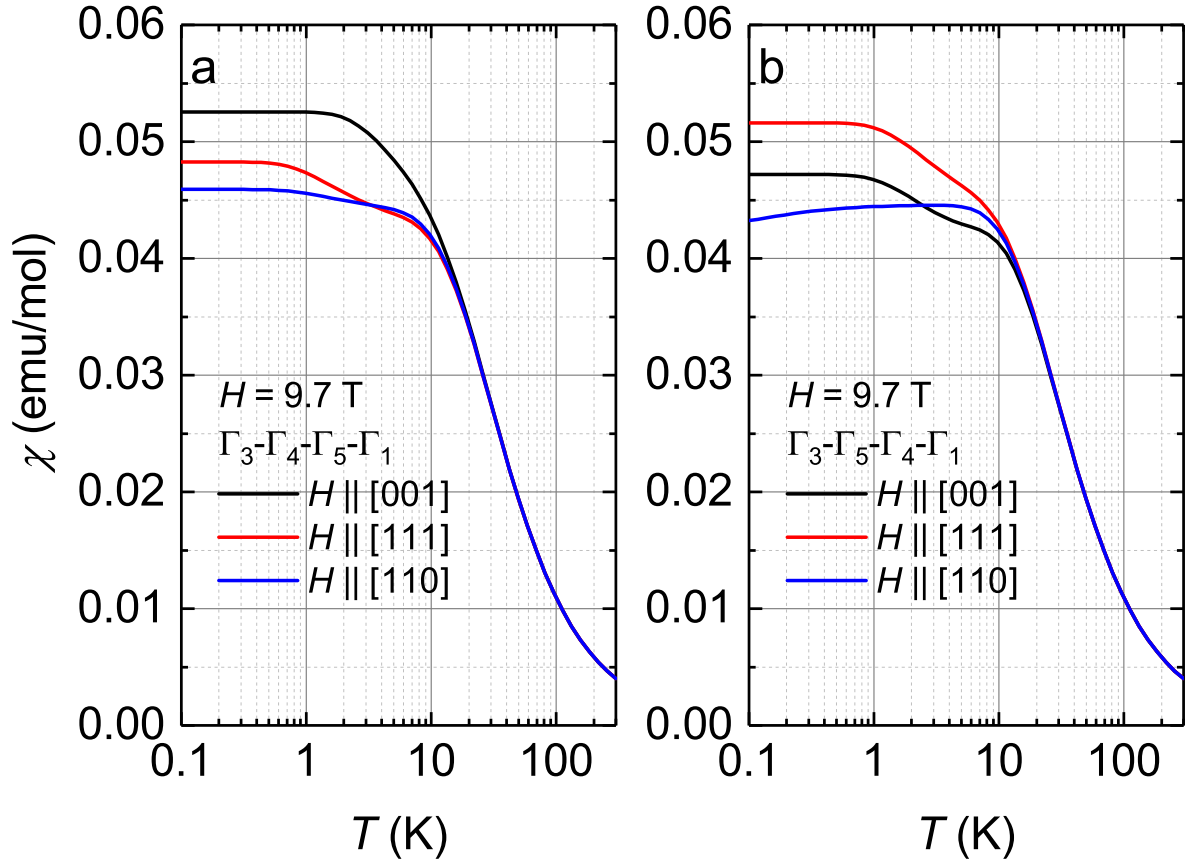


Figure 5.12: Calculated temperature and dependences and anisotropy of χ in $\text{PrNb}_2\text{Al}_{20}$ at 10 T. (a) Calculation for Γ_3 ground state and Γ_4 first excited state. (b) Calculation for Γ_3 ground state and Γ_5 first excited state. Parameters used for the calculation is same with the ones used in §5.1.

Shown in Fig.5.12(a,b) is the calculated temperature dependences of the susceptibility at 9.7 T, in which the CEF parameters $W = -0.73$ K and $x = 0.44$ are used for the Γ_3 - Γ_4 model, and $W = -0.90$ K and $x = -0.50$ are used for the Γ_3 - Γ_5 model obtained from the magnetization analysis in §5.1. μ_{eff} and λ are the same values with the previous analysis used in §5.1. As shown in Fig.5.12, $\langle 100 \rangle$ directions are the easiest magnetization axes at low temperatures and high fields when the first excited state is the Γ_4 triplet. Meanwhile, $\langle 111 \rangle$ directions are the easiest axes when the Γ_5 is the first excited state, which is consistent with the present NMR line profile. Notably, the $\langle 111 \rangle$ directions become the easiest axis only if the ground state is the Γ_3 and the first excited state is the Γ_5 . Then, we concluded that the CEF ground state is the Γ_3 doublet and the first excited state is the Γ_5 triplet in $\text{PrNb}_2\text{Al}_{20}$.

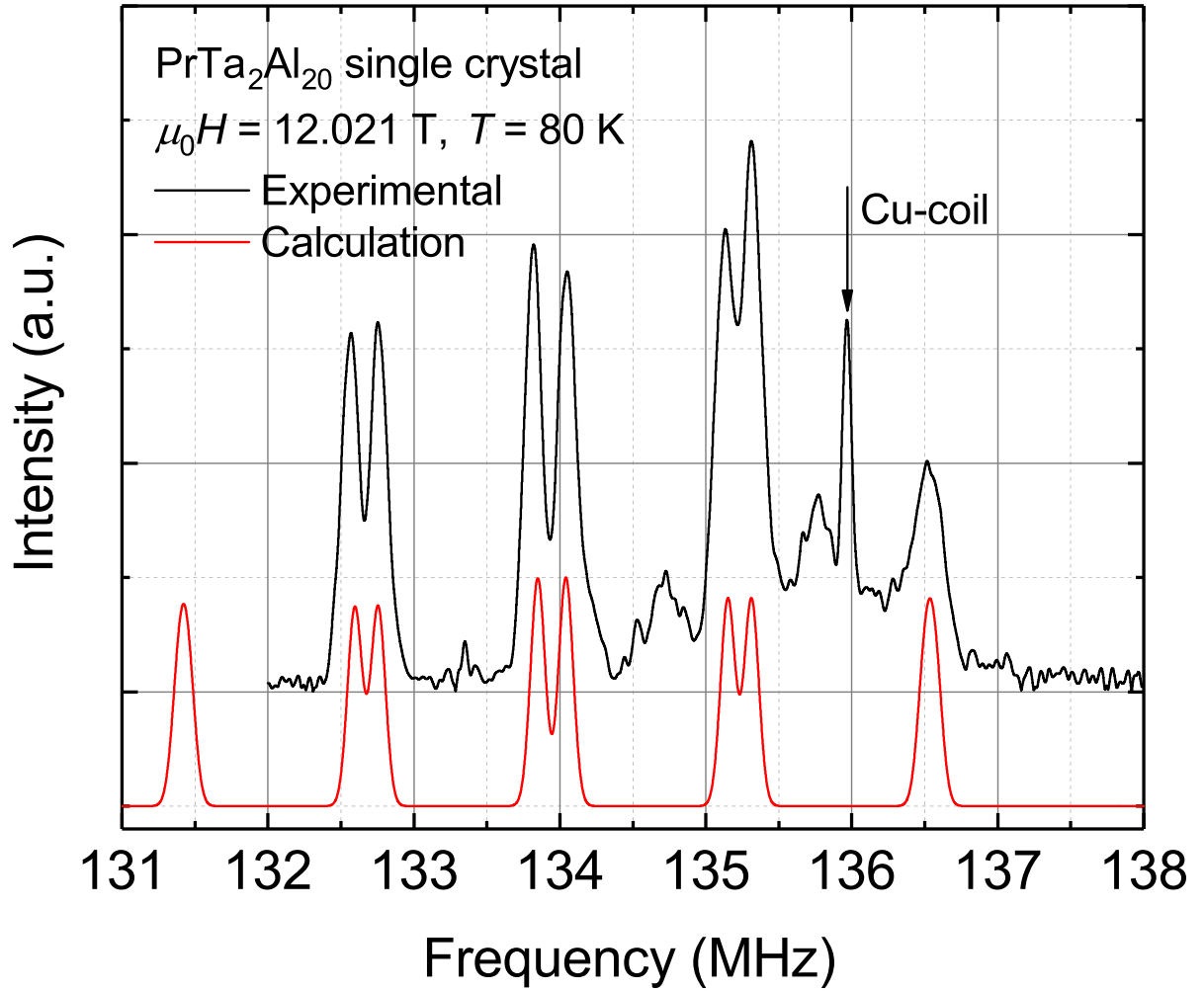


Figure 5.13: NMR spectrum of the Al 48*f* site obtained for single crystal PrTa₂Al₂₀ at $\mu_0 H = 12.021$ T, 1.7 K. The red line is the calculated lines of the Al 48*f* site for $H \parallel [111]$.

The black solid line in Fig. 5.13 shows the ²⁷Al-NMR spectrum obtained for a single crystal at 12.021 T and at 1.7 K. Prior to the measurement, a mechanical shock is applied to align the sample to its easy axis direction. The red solid line is the calculated spectrum by using the NQR parameters of Al 48*f* site obtained in §5.2.1 assuming $H \parallel \langle 111 \rangle$. The structure of NMR line profile is well reproduced by the simulation. Then, the easy-axis direction is determined to be parallel to one of the $\langle 111 \rangle$ directions. By using the similar considerations in PrNb₂Al₂₀ case, the CEF ground state and first excited state in PrTa₂Al₂₀ are determined to be the Γ_3 doublet and the Γ_5 triplet, respectively.

5.3.2 Knight shift measurements of $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

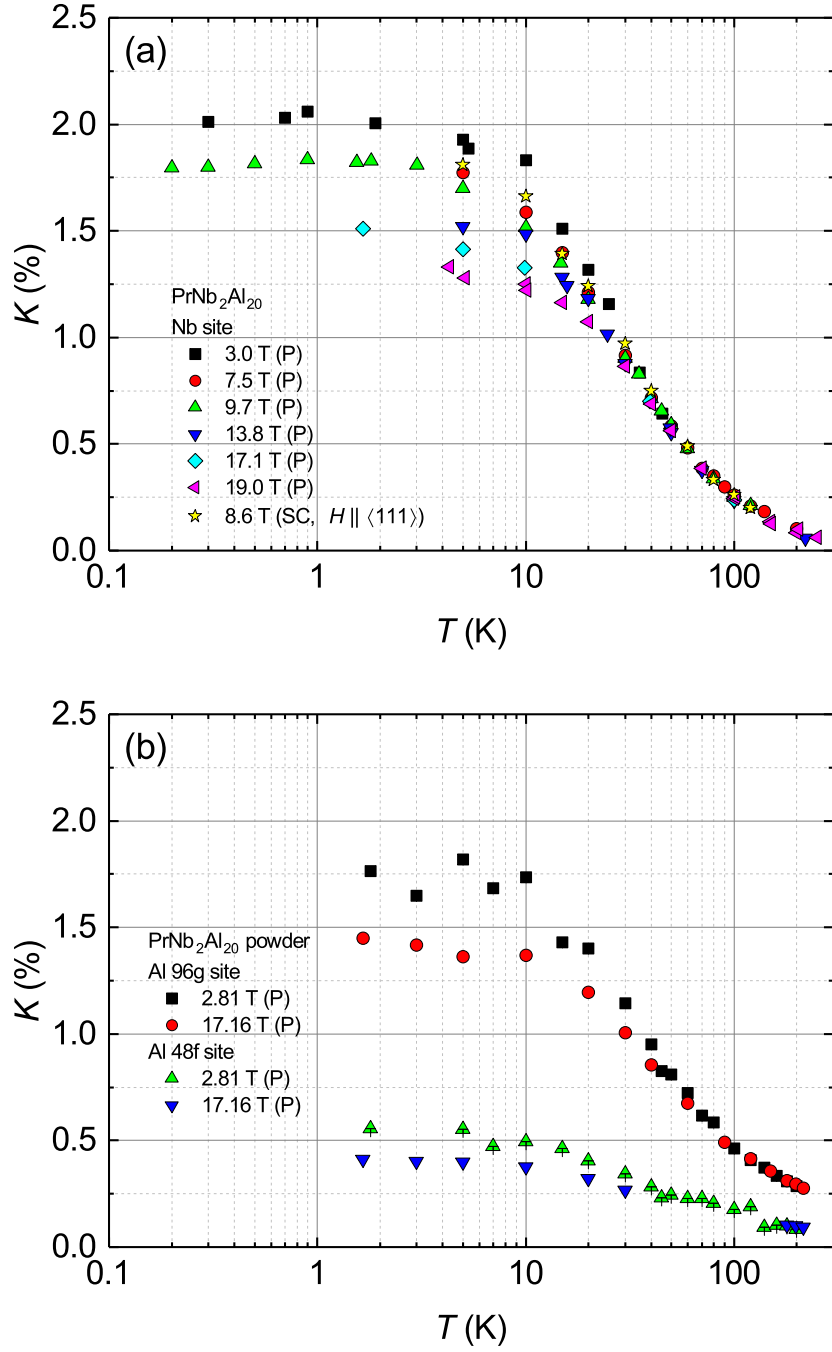


Figure 5.14: (a) The temperature and field dependences of the ^{93}Nb -NMR Knight shift obtained for the powder (P) and for single crystal (SC) samples. For the single crystal measurement, the magnetic field is applied parallel to one of the $\langle 111 \rangle$ directions. (b) The temperature and field dependence of the ^{27}Al -NMR Knight shift obtained for the powder sample and for Al 96g and 48f sites.

Next, we discuss about the c - f hybridization in $\text{PrNb}_2\text{Al}_{20}$ through the Knight shift measurements. Shown in Fig. 5.14(a,b) are the temperature and field dependences of K_{iso} , that are obtained from the shift of the NMR lines for the powder and single crystal samples. K_{iso} is defined by the shift of the center of mass of the NMR spectrum as:

$$K_{\text{iso}} \equiv \frac{\omega_c - \omega_0}{\omega_0}, \quad (5.5)$$

where ω_c are the center of mass of NMR spectrum, and $\omega_0 \equiv \gamma_n H_0$ is the resonance frequency for bare nuclei. The overall feature of K_{iso} is similar to the susceptibility reported previously [11], and supports that the microscopic shift certainly reflects the bulk magnetic behavior, while the magnitude of K_{iso} is different for each of the ligand sites. This difference reflects the magnitude of the hyperfine coupling between the Pr $4f$ moments and ligand nuclei. K_{iso} of Al 96g site is much larger than of Al 48f site. This behavior is qualitatively the same to the ^{27}Al -NMR results in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V}$) [56]. K_{iso} is almost field independent above 30 K while it becomes dependent on field below 30 K. As discussed later, the suppression of K_{iso} with increasing magnetic field can be reproduced by a CEF model for the localized $4f$ electrons in the $4f^2$ configuration.

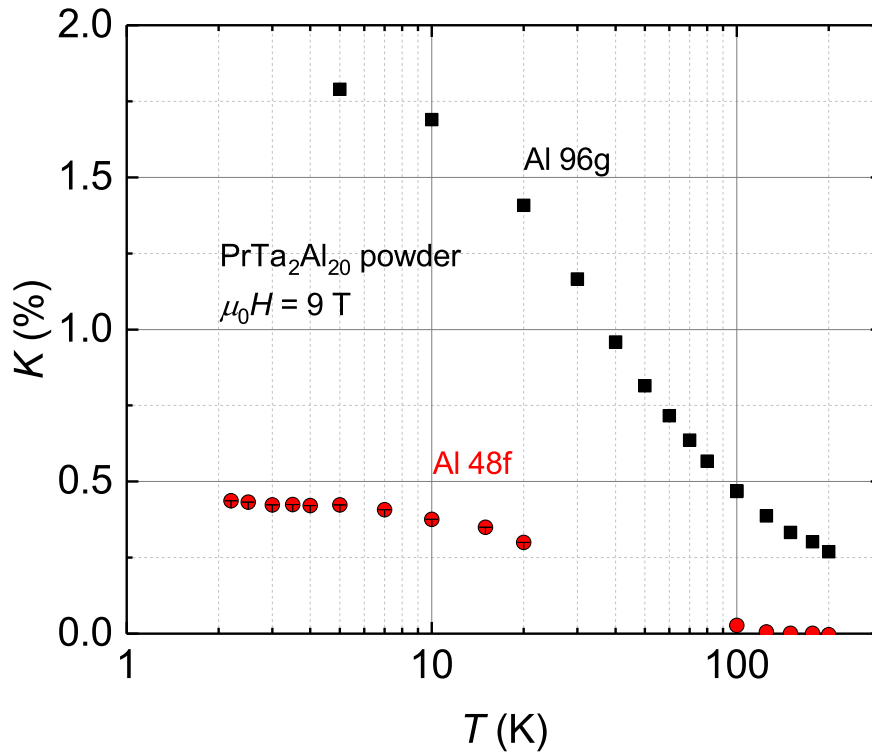


Figure 5.15: Temperature dependence of the Knight shift obtained for $\text{PrTa}_2\text{Al}_{20}$ powder at 9 T.

Figure 5.15 shows the temperature dependence of the Knight shift K obtained for $\text{PrTa}_2\text{Al}_{20}$ powder at 9 T. K is determined by the shift of the center of mass of the ^{27}Al central transition. Between 20 and 100 K, the accidental overlapping of the Al $4f$ line and the impurity lines prevents us to extract K . The overall temperature dependence is quite similar to other $\text{PrT}_2\text{Al}_{20}$ systems, and suggests the nonmagnetic ground state of $4f$ electrons.

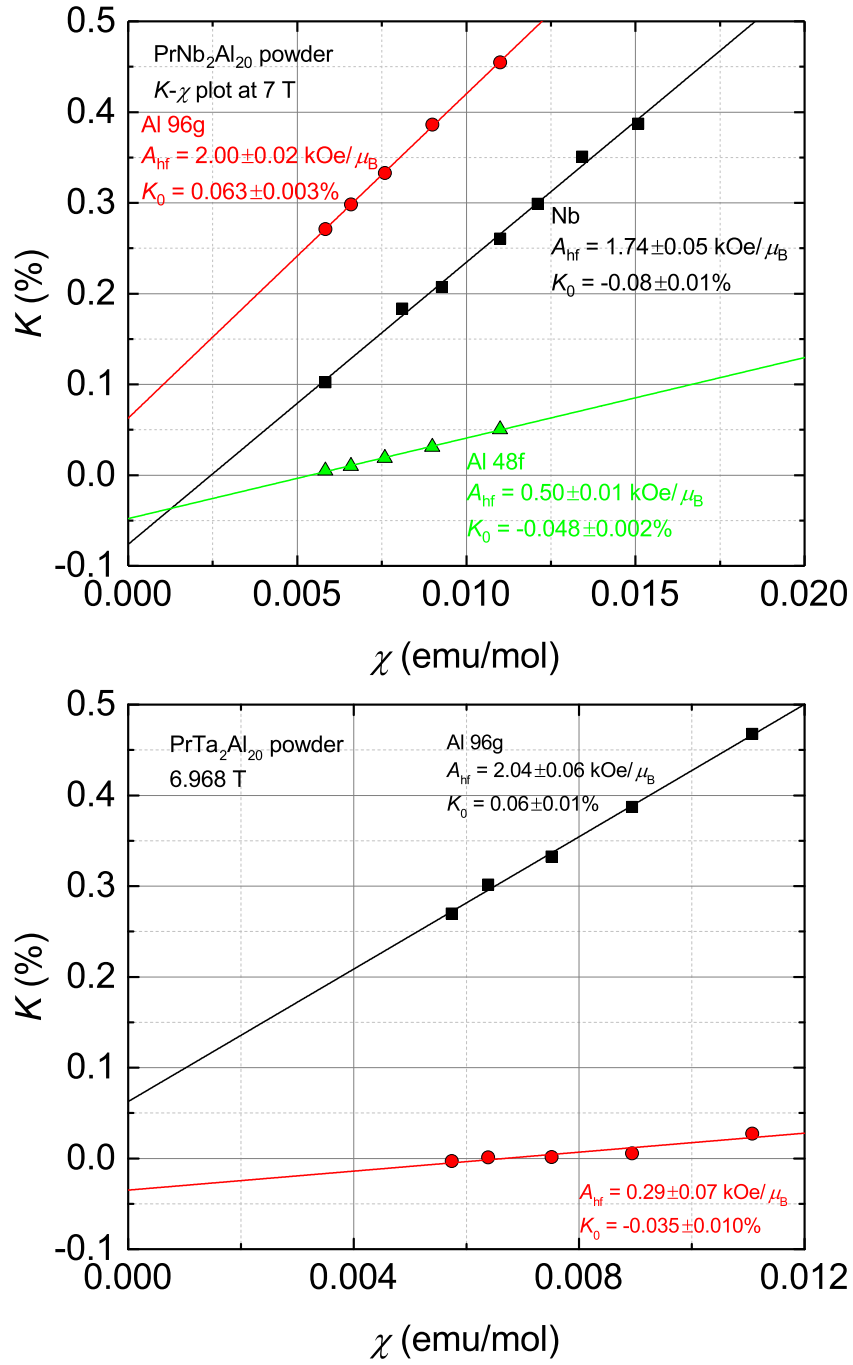


Figure 5.16: (upper) The K - χ plot for PrNb₂Al₂₀ with temperature as an implicit parameter at 7 T. χ is obtained for randomly oriented ten single crystals at 7 T [11]. The solid lines are the result of least-squares fitting. The fitting range is between 70 and 200 K. (lower) The K - χ plot for PrTa₂Al₂₀ with temperature as an implicit parameter at 7 T. χ is obtained for a polycrystal sample [23]. The solid lines are the result of least-squares fitting. The fitting range is between 100 and 200 K.

Figure 5.16 shows the K_{iso} versus χ plot for $\text{PrNb}_2\text{Al}_{20}$ and for $\text{PrTa}_2\text{Al}_{20}$ with temperature as an implicit parameter. Here K_{iso} 's and χ are obtained at 7 T. χ for $\text{PrNb}_2\text{Al}_{20}$ is obtained by using unaligned ten single crystals and that for $\text{PrTa}_2\text{Al}_{20}$ is obtained by using polycrystal samples [11, 23]. K_{iso} and χ can be decomposed into

$$K_{\text{iso}}(T, H) = K_{\text{CW}}(T, H) + K_0(H) \quad (5.6)$$

$$\chi(T, H) = \chi_{\text{CW}}(T, H) + \chi_0(H). \quad (5.7)$$

$\chi_{\text{CW}}(T, H)$ is the temperature and field dependent magnetic susceptibility of $4f$ electrons and includes temperature-dependent Van Vleck term. χ_0 is the total contribution of the Pauli, orbital, core electron, and temperature independent Van Vleck contributions. The plot shows a good linear relation and the slope yields the hyperfine coupling constants A_{hf} at the ligand sites as follows:

$$K(T, H) = \frac{A_{\text{hf}}}{N_A \mu_B} \chi_{\text{CW}}(T, H) + K_0(H). \quad (5.8)$$

The dashed lines in Fig. 5.16 are the result of the least-squares fitting above 70 K. The obtained A_{hf} 's and K_0 's are summarized in Tables 5.4.

Site	A_{hf} (kOe / μ_B)	K_0 (%)	A_{dip} (kOe / μ_B , cal)
Nb	1.74 ± 0.05	0.02 ± 0.01	0.16
Al 96g	2.00 ± 0.02	0.063 ± 0.003	0.46
Al 48f	0.50 ± 0.01	-0.048 ± 0.021	0.13

Site	A_{hf} (kOe / μ_B)	K_0 (%)	A_{dip} (kOe / μ_B , cal)
Al 96g	2.04 ± 0.06	0.06 ± 0.01	0.46
Al 48f	0.29 ± 0.07	-0.035 ± 0.010	0.13

Table 5.4: A_{hf}^i and K_0^i obtained from the K - χ plot for (upper) $\text{PrNb}_2\text{Al}_{20}$ and (lower) $\text{PrTa}_2\text{Al}_{20}$. The calculated maximum principal values of A_{dip} 's are also shown.

In general, A_{hf} includes the transferred hyperfine interaction A_{tr} which relates the local spin density at the ligand site transferred through the c - f hybridizations and the classical dipole interaction A_{dip} created by the localized $4f$ electrons, then, A_{hf} can be written as $A_{\text{hf}} = A_{\text{tr}} + A_{\text{dip}}$. A_{dip} is calculated in the same way in § 5.3 and is shown in Table 5.4. Here we listed the maximum principal values of A_{dip} , though A_{dip} is basically a tensor. A_{hf} 's are much greater than A_{dip} 's for all of the observed sites, and are suggested to be dominated by the transferred hyperfine interaction. In fact, Tokunaga *et al.* reported A_{hf} is larger than A_{dip} at the Al 96g and 48f sites from the ^{27}Al -NMR measurements of single crystal $\text{PrT}_2\text{Al}_{20}$ (T

= Ti, V) [56]. Thus, the present result indicates that the local spin density at ligand sites is enhanced through the strong c - f hybridization in $\text{PrNb}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$.

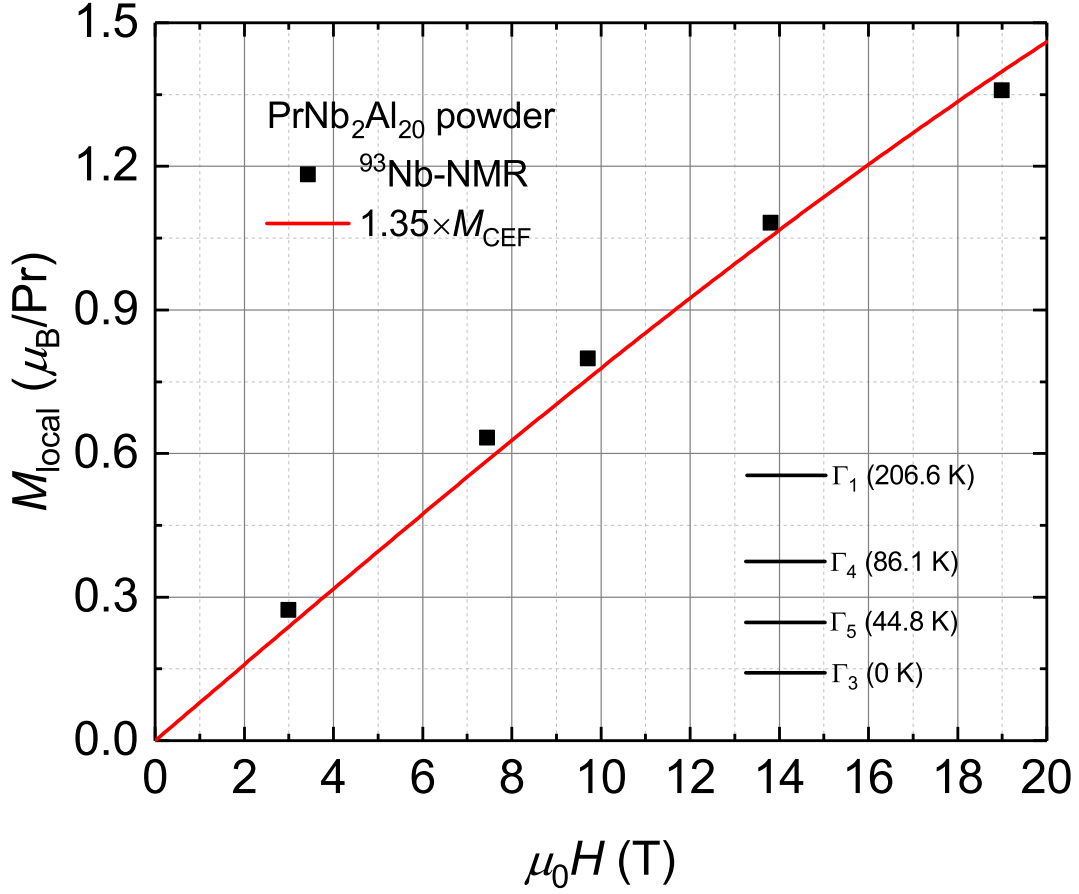


Figure 5.17: Field dependence of the magnetization M_{local} estimated from the NMR Knight shift K_{iso} at Nb site at 10 K. The Red solid line is the fitting based on the CEF model. Inset: the CEF scheme used for the calculation.

Shown in Fig.5.17 is the field dependence of the local magnetization $M_{\text{local}} = (N_A \mu_B K_{\text{iso}} H) / A_{\text{hf}}$ estimated from A_{hf} and K_{iso} at 15 K between 3 and 19 T. As reported previously in the bulk magnetization measurement at 2 K [11], M_{local} deviates from linearity at high fields. By using Eqs. (5.1,5.2), we calculated the bulk magnetization $M_{\text{CEF}} = \chi_{\text{CEF}} H$. The red solid line is the result of the calculation multiplied by 1.35. For the calculation, $W = -2.87$ K and $x = 0.60$ is used that are recently reported by Iwasa *et al.* from the inelastic neutron diffraction measurement [26]. In the present calculation, we used μ_{eff} and λ used for the previous calculation and the calculation is performed self-consistently. The field dependence agrees qualitatively though the absolute value is not reproduced.

5.4 Dynamical properties of $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

5.4.1 NMR longitudinal relaxation rate $1/T_1$ in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

First, we discuss the relaxation process in $\text{PrT}_2\text{Al}_{20}$. The recovery curve of the nuclear magnetization may be written as:

$$M(t) = M_\infty - M_0 \sum_i \alpha_i \exp(-\beta_i t/T_1). \quad (5.9)$$

$M(t)$ is the magnitude of the nuclear magnetization, M_∞ is the magnetization at the thermal equilibrium, M_0 is the magnetization just after the inversion pulse, and α_i and β_i are the coefficients determined by the transition and the relaxation process.

The longitudinal relaxation process in $\text{PrT}_2\text{Al}_{20}$ is not simple. That is, $4f$ electric quadrupole fluctuation as well as magnetic dipole/octupole fluctuation causes the relaxation because the Γ_3 state has two quadrupoles and one octupole, and the Γ_4 and Γ_5 states have dipole and five quadrupoles at zero fields.

In general, magnetic fluctuation causes the relaxation between nuclear spin levels $|m\rangle \leftrightarrow |m \pm 1\rangle$. Then the transition probability for a magnetic origin is given by [59, 60]

$$W_{m,m\pm 1}^m = W_0(I \mp m)(I \pm m + 1). \quad (5.10)$$

On the other hand, the electric fluctuation causes the electric quadrupole relaxation between nuclear spin levels of $m \leftrightarrow m \pm 1$ and $m \leftrightarrow m \pm 2$ through the fluctuation of the EFG. The transition probabilities for an electric origin are given by [59, 60]

$$W_{m,m\pm 1}^q = W_1(2m \pm 1)^2(I \mp m)(I \pm m + 1)/[2I(2I - 1)^2] \quad (5.11)$$

$$W_{m,m\pm 2}^q = W_2(I \mp m)(I \pm m + 1)[I \mp (m \pm 1)][I \pm (m \pm 1) + 1]/[2I(2I - 1)^2]. \quad (5.12)$$

Here W_0 , W_1 , and W_2 are constant values related to the relaxation time T_1 .

All of the relaxation curves obtained at the Nb site in $\text{PrNb}_2\text{Al}_{20}$ can be fitted by the curve for a magnetic origin. For such a case, α_i and β_i is given by Narath [61]. For the central line of ^{93}Nb -NMR ($I = 9/2$),

$$\frac{M_\infty - M(t)}{M_0} = \frac{1}{165}e^{-t/T_1} + \frac{24}{715}e^{-6t/T_1} + \frac{6}{65}e^{-15t/T_1} + \frac{1568}{7293}e^{-28t/T_1} + \frac{7938}{12155}e^{-45t/T_1}. \quad (5.13)$$

and for the second satellite line,

$$\frac{M_\infty - M(t)}{M_0} = \frac{1}{165}e^{-t/T_1} + \frac{1}{66}e^{-3t/T_1} + \frac{2}{2145}e^{-6t/T_1} + \frac{10}{143}e^{-10t/T_1} + \frac{5}{78}e^{-15t/T_1} \quad (5.14)$$

$$+ \frac{2}{165}e^{-21t/T_1} + \frac{2048}{7293}e^{-28t/T_1} + \frac{288}{715}e^{-36t/T_1} + \frac{360}{2431}e^{-45t/T_1}. \quad (5.15)$$

The field dependence of $1/T_1$ is small between 3 and 19 T and this small field dependence is clearly different from the behavior of $\text{PrOs}_4\text{Sb}_{12}$ [62] and $\text{PrTi}_2\text{Al}_{20}$ [56] having the nonmagnetic CEF ground state. $1/T_1$ in nonmagnetic $\text{LaNb}_2\text{Al}_{20}$ shows T -linear behavior between 5 and 120 K as expected to the normal metal. Below 100 K, $1/T_1$ in $\text{PrNb}_2\text{Al}_{20}$ is enhanced with respect to $\text{LaNb}_2\text{Al}_{20}$ and shows $1/T_1 \propto T^\alpha$ ($\alpha \approx 2/3$) behaviors. Then, $4f$ electronic fluctuations is certainly responsible to this enhancement. Below 2 K, the exponent of $1/T_1$ gradually decreases with decreasing temperatures.

At the Al 96g site in $\text{PrNb}_2\text{Al}_{20}$ and at low fields and high temperatures, $1/T_1$ can be fitted by the magnetic relaxation curve

$$\frac{M_\infty - M(t)}{M_0} = \frac{1}{35}e^{-t/T_1} + \frac{8}{45}e^{-6t/T_1} + \frac{50}{63}e^{-15t/T_1}. \quad (5.16)$$

At high fields and low temperatures, the recovery curve deviates from the magnetic relaxation, possibly due to the development of the magnetic anisotropy as discussed in §5.1. So that, the recovery curves are tentatively fitted by Eq. (5.16) to extract the powder averaged $1/T_1$. $1/T_1$ in $\text{LaNb}_2\text{Al}_{20}$ shows T -linear behavior of $1/T_1 = 0.179T$ as expected to the normal metal. At 3 T and above 30 K, the temperature dependence of $1/T_1$ becomes smaller with increasing temperatures, possibly relates to the CEF gap between the ground and first excited states. At 17 T and above 20 K, $1/T_1$ is suppressed than the value of the lower fields.

Similar to the case of $\text{PrNb}_2\text{Al}_{20}$, the recovery curves obtained at Al 96g site in $\text{PrTa}_2\text{Al}_{20}$ are well fitted by Eq. 5.16 at high temperatures but deviates from it at lower temperatures and high fields. Then, the recovery curve is analyzed by the same manner in $\text{PrNb}_2\text{Al}_{20}$ to extract the powder averaged $1/T_1$. Above 50 K, $1/T_1$ slightly suppressed with increasing magnetic field. Below 10 K, in contrast to the case for $T = \text{Nb}$, $1/T_1$ is enhanced with increasing magnetic field and decreases suddenly at around 1 K, suggesting a phase transition. Such an enhancement and sudden decrease is reported at around the quadrupole ordering temperature in ^{27}Al -NMR at Al 96g site in $\text{PrTi}_2\text{Al}_{20}$ [56].

5.4.2 Analysis of NMR longitudinal relaxation rates $1/T_1$ in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$)

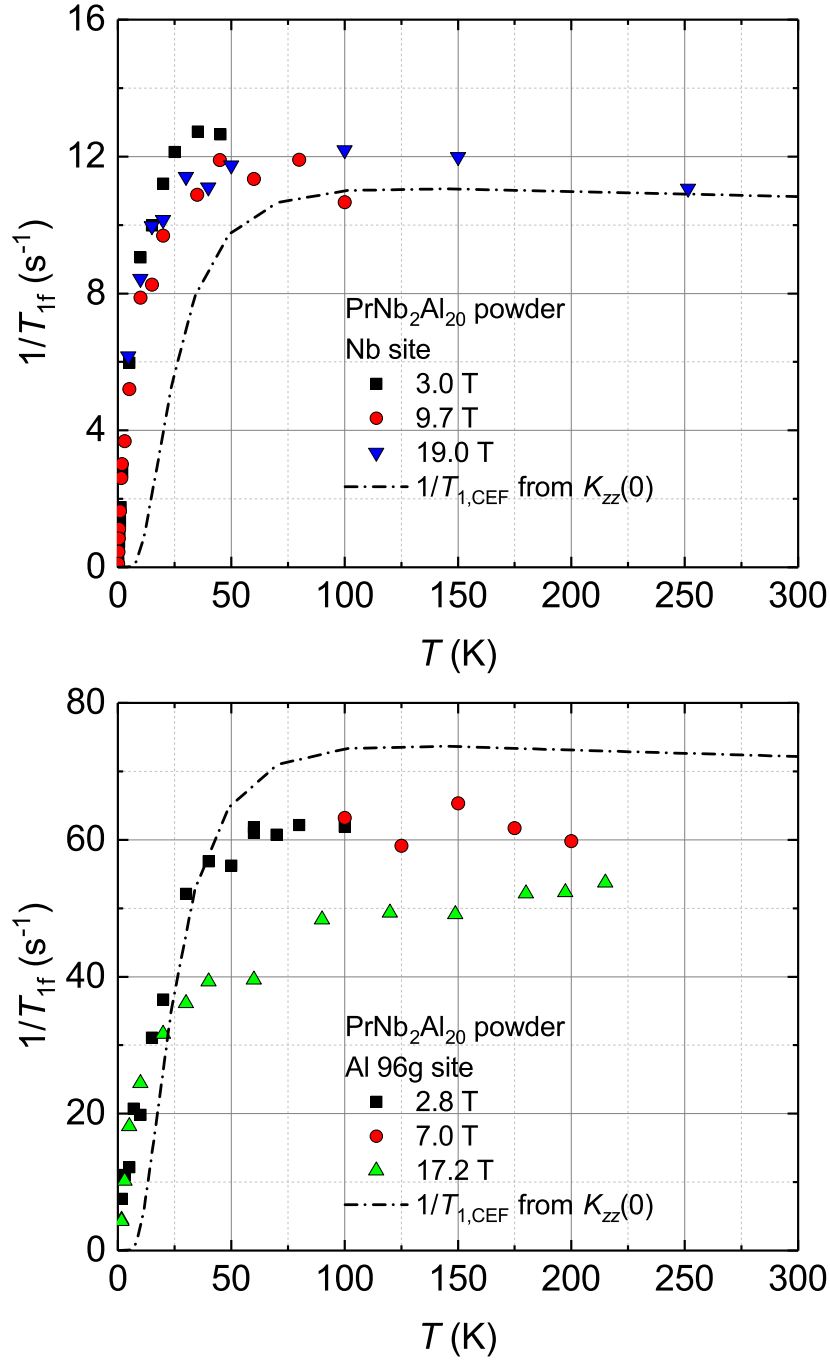


Figure 5.18: Temperature and field dependences of the $4f$ electronic contributions for $1/T_1$ at (Upper) Nb site and (Lower) at Al 96g site in $\text{PrNb}_2\text{Al}_{20}$. Black dash-dotted lines are the calculated contribution of the CEF states $1/T_{1,\text{CEF}}$ as discussed in §5.24, which is based on a simple assumption described in the text. The model used for the calculation is expanded to include the field dependence. Details are shown in the text.

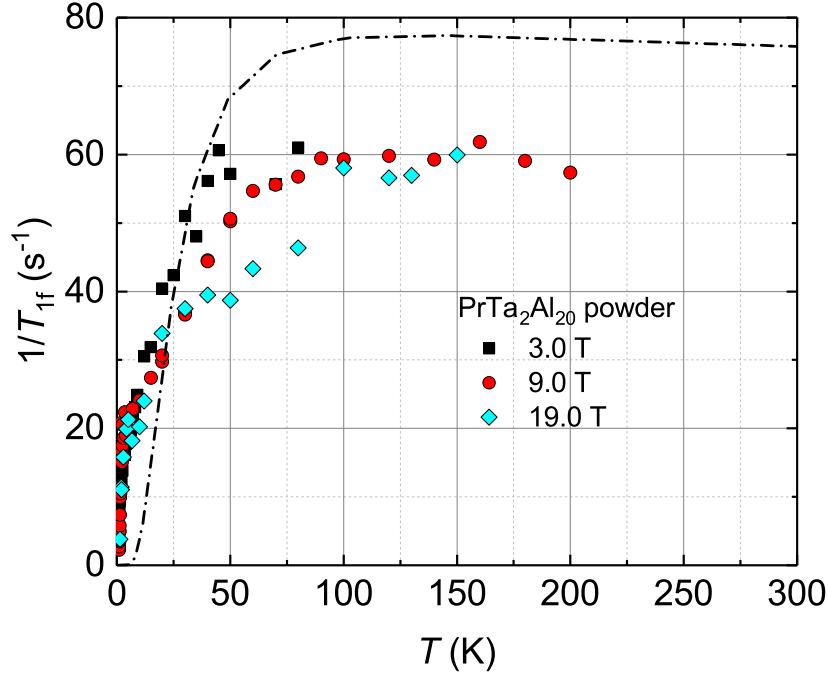


Figure 5.19: Temperature and field dependences of the $4f$ electronic contributions for $1/T_1$ at Al 96g site in $\text{PrTa}_2\text{Al}_{20}$. Black dash-dotted lines are the calculated contribution of the CEF states $1/T_{1,\text{CEF}}$ as discussed in §5.24. Details are described in the text.

Figures 5.18 and 5.19 show the temperature and field dependences of the $4f$ electronic contributions of $1/T_1$, $1/T_{1f}$ at Nb site in $\text{PrNb}_2\text{Al}_{20}$ and at Al 96g sites in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Nb, Ta}$). $1/T_{1f}$ is defined as $1/T_{1f} \equiv 1/T_1 - 1/T_{1,\text{La}}$. Above ≈ 50 K, the $1/T_{1f} \approx \text{const.}$ behavior is observed. Such a behavior indicates $4f$ electrons are well localized at high temperatures. Below ≈ 50 K, $1/T_{1f}$ decreases with decreasing temperature, which is related to the population change of the CEF excited states [56, 63]. With increasing the magnetic field, $1/T_{1f}$ is remarkably suppressed at Al 96g site above ≈ 30 K which might be originate from the field dependence of the CEF states. The amount of the suppression of $1/T_{1f}$ at Nb site is much smaller than at Al 96g site. It might be related with the facts that Al ions at the 96g sites are much closer to Pr ions than Nb ions and reflect the CEF state of the localized $4f$ electrons. The dashed-dotted lines in Figs. 5.18 and 5.19 is the result of the calculation based on the simple localized CEF model used by Tanida *et al.* to analyze the temperature dependence of $1/T_1$ [63]. In these calculations, the field effect on the CEF state is not included for the simplicity. We discuss the detail of the calculation in §5.24.

In addition, the suppression of the relaxation rate with increasing magnetic field is opposite to the tendency of the magnetic field dependence of $1/T_1$ at low temperatures in $\text{PrTi}_2\text{Al}_{20}$ [56]. We discuss about these facts in the following section.

5.4.3 Magnitude of the c - f hybridization in $\text{PrT}_2\text{Al}_{20}$ estimated from NMR $1/T_1$

In this section, we discuss the c - f hybridization in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V, Nb, Ta}$) from the temperature dependence of $1/T_{1f}$ at high temperatures. First, we try to systematically compare the strength of c - f hybridization in $\text{PrT}_2\text{Al}_{20}$

To investigate the $4f$ electronic fluctuations in $\text{PrT}_2\text{Al}_{20}$ systematically, we compare the $1/T_{1f}$ divided by the square-sum of the $\mathbf{q}$ -dependent hyperfine coupling constant $\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2$ at Al 96g site in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V, Nb, Ta}$). At first, we have to estimate $\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2$ to calculate $1/(T_{1f} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2)$. $\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2$ can be replaced by using A_{tr} and A_{dip} as [63, 64, 65]:

$$\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 = \left(\frac{A_{\text{tr}}^2}{z} + \sum_i A_{\text{dip},i}^2 \right), \quad (5.17)$$

where A_{tr}^2/z is estimated as $(A_{\text{hf}} - A_{\text{dip}})^2/z$ by using A_{hf} 's obtained in the previous section and Ref. [56, 57], in which z is the number of the neighboring Pr ions surrounding the ligand ions. In this estimation, we assume that the first nearest neighboring (NN) Pr ions contribute to the hyperfine coupling. In this case, we take $z = 1$ for Al 96g site and $z = 6$ for Nb site. $\sum_i A_{\text{dip},i}^2$ can be calculated from $\sum_i \mathbf{h}_{\text{dip},i}^2$ as described in § 3. The obtained A_{tr}^2/z and $\sum_i A_{\text{dip},i}^2$ are summarized in Table 5.5.

	A_{tr}^2/z (Oe ²)	$\sum_i A_{\text{dip},i}^2$ (Oe ²)	$\sum_{\mathbf{q}} A_{\mathbf{q}} ^2$ (Oe ²)
PrTi ₂ Al ₂₀	950 ²	$\lesssim 450^2$	$\approx 1050^2$
PrV ₂ Al ₂₀	1480 ²	$\lesssim 450^2$	$\approx 1550^2$
PrNb ₂ Al ₂₀	1540 ²	$\lesssim 450^2$	$\approx 1600^2$
PrTa ₂ Al ₂₀	1680 ²	$\lesssim 450^2$	$\approx 1640^2$
PrNb ₂ Al ₂₀ (Nb)	650 ²	$\lesssim 130^2$	$\approx 660^2$

Table 5.5: A_{tr}^2/z and $\sum_i A_{\text{dip},i}^2$ at Al 96g site in $\text{PrT}_2\text{Al}_{20}$ and at Nb site in $T = \text{Nb}$. The data in $T = \text{Ti, V}$ is taken from Ref. [56].

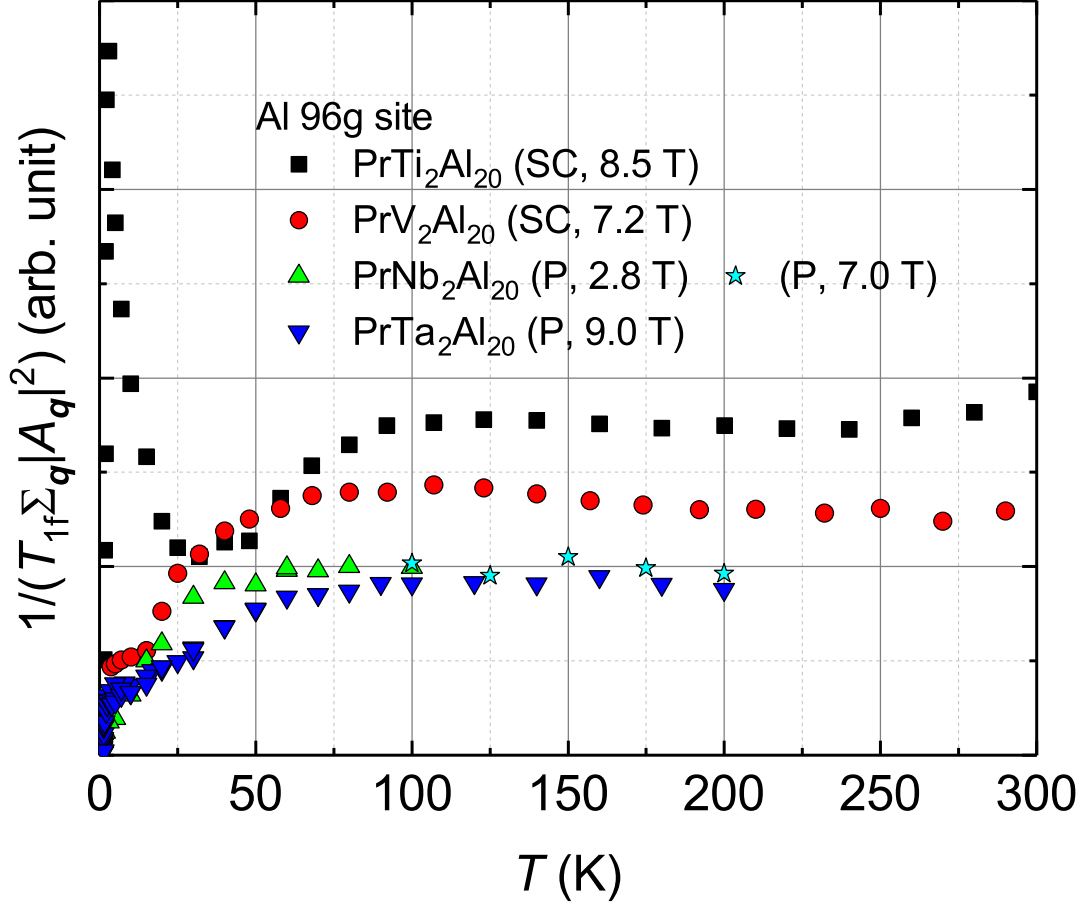


Figure 5.20: Temperature dependence of $1/(T_{1f} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2)$ at Al 96g site in $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti}, \text{Nb}, \text{Ta}$). The data of $T = \text{Ti}, \text{V}$ are taken from Ref. [56].

Figure 5.20 shows the temperature dependence of $1/(T_{1f} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2)$. The data for $T = \text{Ti}, \text{V}$ are taken from Ref. [56].

At high temperatures above ≈ 70 K, $1/(T_{1f} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2) \approx \text{const.}$ behavior is observed for all compounds. In such a case, $4f$ electrons are well localized and $\chi(\mathbf{q}, \omega)$ is dominated by the localized $4f$ electronic magnetic fluctuations through the c - f exchange interactions J_{cf} . In this case, $\mathbf{q}$ -dependence of $\chi(\mathbf{q}, \omega)$ can be ignored and approximated by using the local static susceptibility $\chi(0, 0)$ and the characteristic frequency of the magnetic fluctuation Γ as

$$\chi(\mathbf{q}, \omega) \approx \frac{\chi(0, 0)}{1 - i\omega/\Gamma}, \quad (5.18)$$

where $\chi(0, 0) = \mu_{\text{eff}}^2/3k_B(T - \theta_{\text{CW}})$ and $p_{\text{eff}} = \mu_{\text{eff}}/\mu_B = 3.58$ for a free Pr^{3+} ion. θ_{CW} is obtained from the Curie-Weiss fitting of the bulk magnetic susceptibility above 100 K with fixed $p_{\text{eff}} = 3.58$ as discussed in §2.2.4.

At high temperatures, the magnetic fluctuation rate is expected to be much faster than the NMR frequency, $\Gamma \gg \omega_0$. Then $1/T_1$ is written as [66, 67, 68, 69]:

$$\frac{1}{T_1} \approx \frac{2\gamma_n^2 k_B T}{\mu_B^2} \left(\frac{A_{\text{tr}}^2}{z} + \sum_i A_{\text{dip},i}^2 \right) \frac{\mu_{\text{eff}}^2}{(T - \theta_{\text{CW}})} \frac{1}{\Gamma} \quad (5.19)$$

$$= \frac{2}{3} \gamma_n^2 \left(\frac{A_{\text{tr}}^2}{z} + \sum_i A_{\text{dip},i}^2 \right) p_{\text{eff}}^2 \frac{T}{(T - \theta_{\text{CW}})} \frac{1}{\Gamma}. \quad (5.20)$$

By using this equation, we can estimate the temperature dependent of Γ and can obtain the information of c - f hybridizations. Though we use Eq. (5.20) to estimate Γ in the present analysis, of course we can use the value of the Knight shift K instead of χ because χ and K are connected via the relation $K = (A_{\text{hf}}/N_A \mu_B) \chi$.

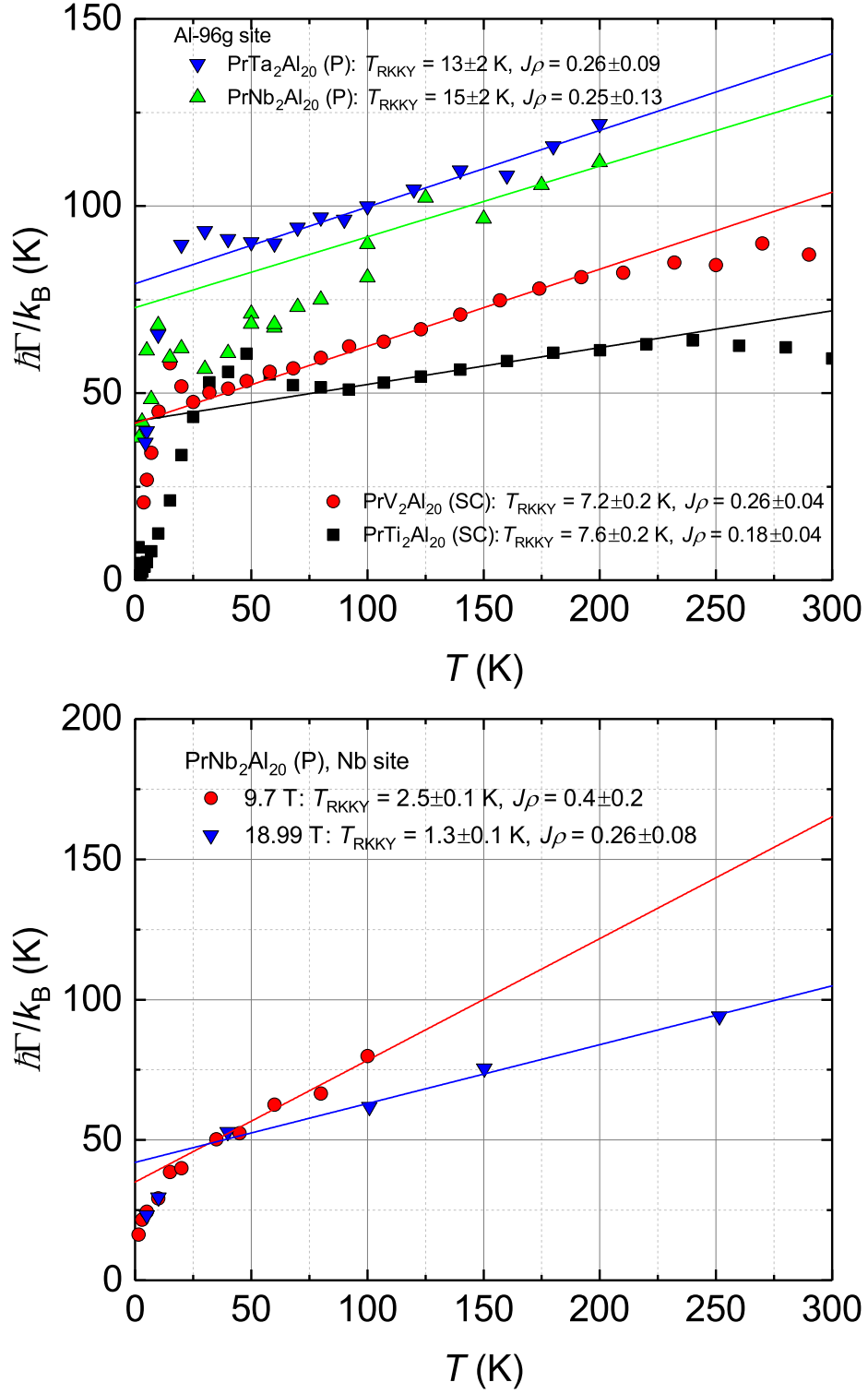


Figure 5.21: Temperature dependence of the spin fluctuation rate Γ estimated from (upper) ^{27}Al - $1/T_{1f}$ measured at Al 96g site in $\Pr\text{T}_2\text{Al}_{20}$ and (lower) ^{93}Nb - $1/T_{1f}$ in $\Pr\text{Nb}_2\text{Al}_{20}$. Solid lines are a least-squares fitting between 100 and 200 K for Al 96g case, and above 50 K for Nb case. T_{RKKY} is defined as $T_{\text{RKKY}} = J_{\text{RKKY}}/k_B$.

Figure 5.21 shows the temperature dependence of Γ in $\text{PrT}_2\text{Al}_{20}$ by using $1/T_{1f}$'s obtained at Al 96g and Nb sites. In these systems, Γ is related to J_{cf} which leads the RKKY interaction and Kondo effect. The RKKY interaction and Kondo effect gives different contribution for the temperature dependence of Γ as $\Gamma_{\text{RKKY}} + \Gamma_{\text{Kondo}}$. Γ_{RKKY} may be expressed as:

$$\Gamma_{\text{RKKY}} = \sqrt{\frac{2z'p_{\text{eff}}^2}{3}} \frac{J_{\text{RKKY}}}{\hbar}, \quad (5.21)$$

in which z' is the number of the interacting nearest neighboring Pr ions, $z' = 4$ in the present case. Note that z' is related to the Pr-Pr interaction. $J_{\text{RKKY}} \propto J_{cf}^2 \rho(E_F) \cos(k_F r)/r^3$, where $\rho(E_F)$ is the density of state at Fermi level, k_F is the Fermi wave vector, r is the distance between Pr ions. Γ_{Kondo} is expressed as

$$\Gamma_{\text{Kondo}} = \frac{\pi}{\hbar} J_{cf}^2 \rho(E_F)^2 k_B T. \quad (5.22)$$

From the least-squares fitting of $\hbar\Gamma/k_B$ at high temperatures above 50 K, $T_{\text{RKKY}} \equiv J_{\text{RKKY}}/k_B$ and $J_{cf}\rho(E_F)$ are estimated. J_{RKKY}/k_B is estimated to be about 1–10 K, which is higher than the ordering temperature $T_Q \lesssim 1$ K. However, this Γ includes the contribution of the CEF excited states, then it might not be directly related to T_Q . $J_{cf}\rho(E_F)$ is different for each compound, and as for $T = \text{Nb}$, it is different from one site to another site. From the ^{27}Al -NMR measurement at Al 96g site, $J_{cf}\rho(E_F) \approx 0.2$ –0.3 is obtained. As for ^{93}Nb -NMR measurement at Nb site for $T = \text{Nb}$, we obtained $J_{cf}\rho(E_F) \approx 0.3$ –0.4. These values are comparable to the values obtained for typical heavy fermion systems [70]. In addition, the obtained $J_{cf}\rho(E_F)$ in $\text{PrT}_2\text{Al}_{20}$ is larger than in the well-localized $4f$ electron system $\text{PrOs}_4\text{Sb}_{12}$ and PrAg_2In , in which $J_{cf}\rho(E_F) \approx 0.05$ and ≈ 0.15 are estimated by using the values of ^{123}Sb -NQR reported by Kotegawa *et al.* [71] and ^{109}Ag -NMR reported by Tanida *et al.* [63], respectively. From the ^{31}P -NMR measurement for a nonmagnetic singlet ground state system $\text{PrFe}_4\text{P}_{12}$ which shows the Kondo effect, a comparable value of $J_{cf}\rho(E_F) \approx 0.213$ is reported by Ishida *et al.* [66]. Therefore, the value of $J_{cf}\rho(E_F) \approx 0.3$ for $\text{PrT}_2\text{Al}_{20}$ at high temperatures suggests a relatively strong Kondo effect in the Pr-based compounds because the magnetic Kondo effect is observed at high temperatures in the Pr-based compounds having $J_{cf}\rho(E_F) \gtrsim 0.2$. The slightly larger Γ for Nb site than Al 96g site in $\text{PrNb}_2\text{Al}_{20}$ suggests the importance of the contribution of d electrons to $\rho(E_F)$ in these compounds suggested by Sakai and Nakatsuji [10], because Nb has four $4d$ electrons though other transition metals have two or three d electrons in $\text{PrT}_2\text{Al}_{20}$.

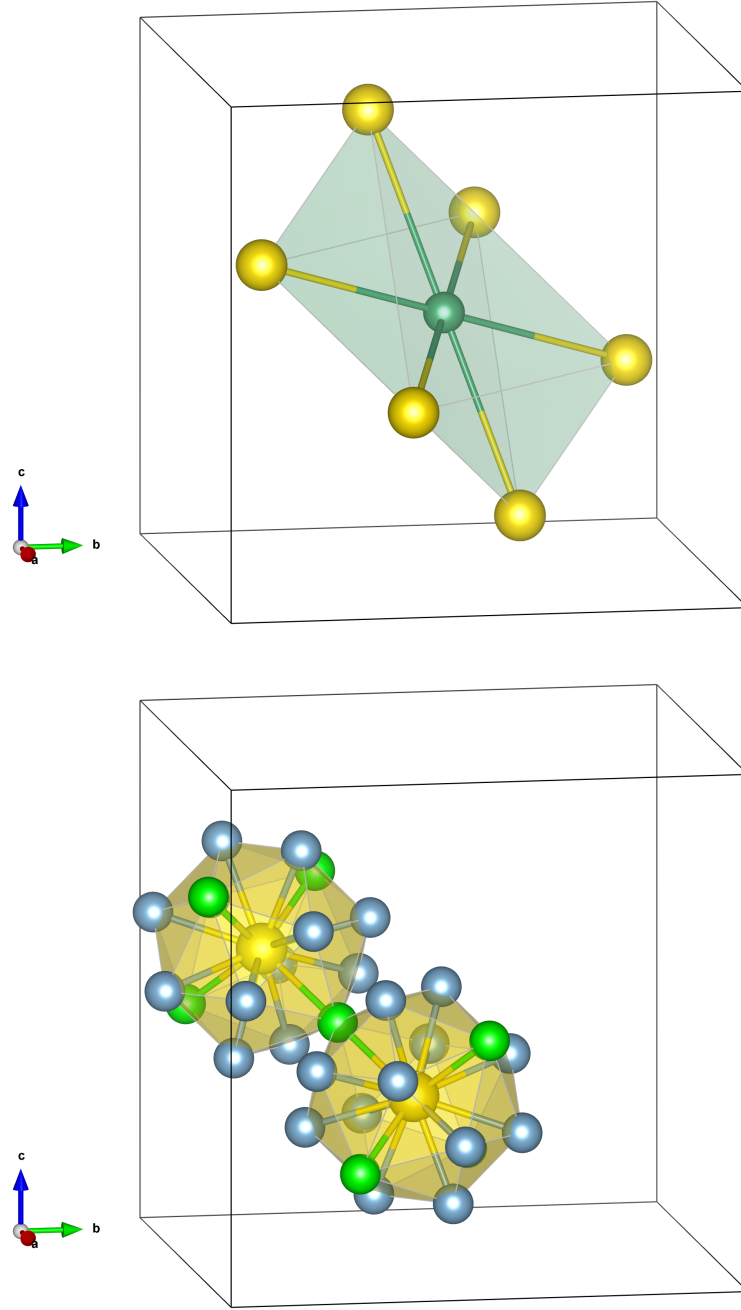


Figure 5.22: (Left) The nearest neighboring Pr ions (yellow) around a specific Nb ion (Green). A Nb site has six nearest neighboring Pr ions. (Right) The Frank-Kasper cage around the two Pr ions formed by Al ions at 16c (light green) and 96g (light blue) sites. Each of Al ions at 96g site has one nearest neighboring Pr ion.

Another possible origin of the large $J_{cf}\rho(E_F)$ is the higher Pr coordination number at Nb site than Al 96g site. As shown in Fig 5.22, a Nb site has six first NN Pr ions while an Al 96g

site has one first NN Pr ions. In addition, a Nb site has eight second NN Pr ions, while an Al 96g site has two second NN Pr ions. Because we assumed that the first NN Pr ions contribute to the hyperfine coupling, $\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2$ for Nb sites might be overestimated, which leads to the overestimation of Γ at the Nb site.

It is useful to estimate the Kondo temperature T_K by using $J_{cf}\rho(E_F)$ obtained above. Yang *et al.* estimated T_K for various $4f$ and $5f$ electron systems, and obtained $J_{cf}\rho(E_F)$ by using the relationship $k_B T_K = W \exp[-1/J_{cf}\rho(E_F)]$, where W is the conduction electron bandwidth [70]. Following their discussion, we systematically estimate T_K by using Γ obtained from $1/T_1$ measurements at the Al 96g site, though there is no straightforward way to obtain T_K for f^2 systems with nonmagnetic ground states. If we assume $W \approx 5000$ K as typical values for p -band and use $J_{cf}\rho(E_F)$'s, we obtain $T_K \approx 18$ K for $\text{PrTi}_2\text{Al}_{20}$. On the other hand, much larger $T_K \approx 85$ K for $\text{PrNb}_2\text{Al}_{20}$ and ≈ 100 K for $\text{PrV}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$ are obtained. The larger value of T_K in $T = \text{V, Nb, and Ta}$ compounds than in $T = \text{Ti}$ compound is consistent with the broader linewidth of the IND spectrum in $\text{PrV}_2\text{Al}_{20}$ and $\text{PrNb}_2\text{Al}_{20}$ than in $\text{PrTi}_2\text{Al}_{20}$, which suggest stronger c - f hybridizations in $\text{PrV}_2\text{Al}_{20}$ and $\text{PrNb}_2\text{Al}_{20}$ than in $\text{PrTi}_2\text{Al}_{20}$ [26, 28, 29]. It is also noteworthy that the larger logarithmic increase in ρ_{4f} in $\text{PrV}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$ than in $\text{PrNb}_2\text{Al}_{20}$ as shown in Fig. 2.2 is consistent with the higher T_K obtained for $\text{PrV}_2\text{Al}_{20}$ and $\text{PrTa}_2\text{Al}_{20}$. Next, let us consider the relationship between T_K and the size of the Frank-Kasper cage. If we define the average distance $d_{\text{av.}}$ between a Pr ion and Al ions surrounding that Pr ion as

$$d_{\text{av.}} = d_{\text{Pr-16c}} \times 4/16 + d_{\text{Pr-96g}} \times 12/16, \quad (5.23)$$

the calculated $d_{\text{av.}}$ and estimated T_K for $T = \text{Ti, V, Nb, and Ta}$ by using the values in §2.2.4 can be summarized in Table 5.6.

	$d_{\text{av.}} [\text{\AA}]$	$T_K [\text{K}]$
$\text{PrTi}_2\text{Al}_{20}$	3.2320	18
$\text{PrV}_2\text{Al}_{20}$	3.2022	100
$\text{PrNb}_2\text{Al}_{20}$	3.2256	85
$\text{PrTa}_2\text{Al}_{20}$	3.2270	100

Table 5.6: The average distance $d_{\text{av.}} = d_{\text{Pr-16c}} \times 4/16 + d_{\text{Pr-96g}} \times 12/16$ between a Pr ion and Al ions forming the Frank-Kasper cage in $\text{PrT}_2\text{Al}_{20}$.

As can be seen in the table, the estimated T_K tends to be higher as the size of the cage becomes smaller. These fact strongly suggests that the obtained T_K certainly reflects the strength of hybridization. The estimated T_K is comparable with the CEF gap size of 40 K, suggesting the degrees of freedom come from the CEF excited states are important to consider

the low temperature physics in $\text{PrT}_2\text{Al}_{20}$.

5.4.4 Analysis of $1/T_1$ based on the localized $4f$ model

From the analysis in the previous section, it is revealed that $4f$ electrons in $\text{PrT}_2\text{Al}_{20}$ are well localized at high temperatures and strongly interact with conduction electrons. Next, we try to separate the contribution of the localized $4f$ dipole fluctuations from $1/T_{1f}$ to extract the contribution of c - f hybridization and/or multipole fluctuations.

Let us consider the temperature dependence of $1/T_{1f}$ based on the localized $4f$ model [63, 65, 72, 73]. As discussed in §3.3, $1/T_1$ can be written as:

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2} [K_{xx}(\omega_0) + K_{yy}(\omega_0)]. \quad (5.24)$$

When the $4f$ electronic fluctuation Γ is much faster than ω_0 as in the present case, we can approximate $K_{xx}(\omega_0) \approx K_{yy}(\omega_0) \approx K_{zz}(\omega_0) \approx K_{zz}(0)$ in the absence of the magnetic field. $K_{zz}(0)$ and $1/T_{1,\text{CEF}}$ can be calculated as

$$K_{zz}(0) = \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \frac{1}{Z} \sum_{\alpha,i} e^{-E_{\Gamma_\alpha^i}/k_B T} \frac{|\langle \Gamma_\alpha^i | J_z | \Gamma_\alpha^i \rangle|^2}{\Gamma} \quad (5.25)$$

$$\frac{1}{T_{1,\text{CEF}}} = \gamma_n^2 K_{zz}(0) \quad (5.26)$$

$$= \frac{\gamma_n^2}{\Gamma} \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \frac{1}{Z} \sum_{\alpha=4,5} e^{-E_{\Gamma_\alpha^i}/k_B T} |\langle \Gamma_\alpha^i | J_z | \Gamma_\alpha^i \rangle|^2, \quad (5.27)$$

where $Z = \sum_{\alpha,i} \exp(-E_{\Gamma_\alpha^i}/k_B T)$ is the single ion partition function, i is the index to specify the degenerated CEF states, Γ is the frequency of $4f$ electronic fluctuation frequency. In the absence of the magnetic field, only $\langle \Gamma_\alpha^i | J_z | \Gamma_\alpha^i \rangle$'s are nonzero for Γ_4 and Γ_5 triplets, in which $|\langle \Gamma_4^i | J_z | \Gamma_4^i \rangle| = 0.5$, and $|\langle \Gamma_5^i | J_z | \Gamma_5^i \rangle| = 2.5$. Then, Eq. (5.24) expresses that the contribution of the magnetic fluctuations arising from the thermally excited CEF states for $1/T_{1f}$.

To calculate $E_{\Gamma_\alpha^i}$'s, we used $W = -2.87$ K and $x = -0.60$ obtained from the inelastic neutron scattering experiment [26]. The magnetic anisotropy indicates that the low lying CEF scheme is Γ_3 – Γ_5 for $\text{PrTa}_2\text{Al}_{20}$, we tentatively used the same CEF parameters and calculated $1/T_{1,\text{CEF}}$ for $\text{PrTa}_2\text{Al}_{20}$. The calculated $1/T_{1,\text{CEF}}$ is shown by the black dash-dotted lines in Figs. 5.18.

Here, Γ is taken to be $\hbar\Gamma/k_B = 20$ K which corresponds to the HWHM of the inelastic neutron diffraction measurement [26]. This value is consistent with the above estimation of Γ

from $1/T_1$. Above 50 K, especially for the Al 96g site at low fields, the temperature independent behavior above ≈ 70 K and sudden decrease below 50 K are well reproduced. In addition, the absolute value of $1/T_{1f}$ is in agreement with the experimental results at high temperatures though we roughly assumed that only the nearest neighboring $4f$ electrons contribute to A_{tr} . However, one cannot explain the suppression at high field and enhancement at low temperatures of $1/T_{1f}$ in this model.

In the above discussion, we ignored the field dependence of the CEF states. Next, we take the field effect for the CEF states into account.

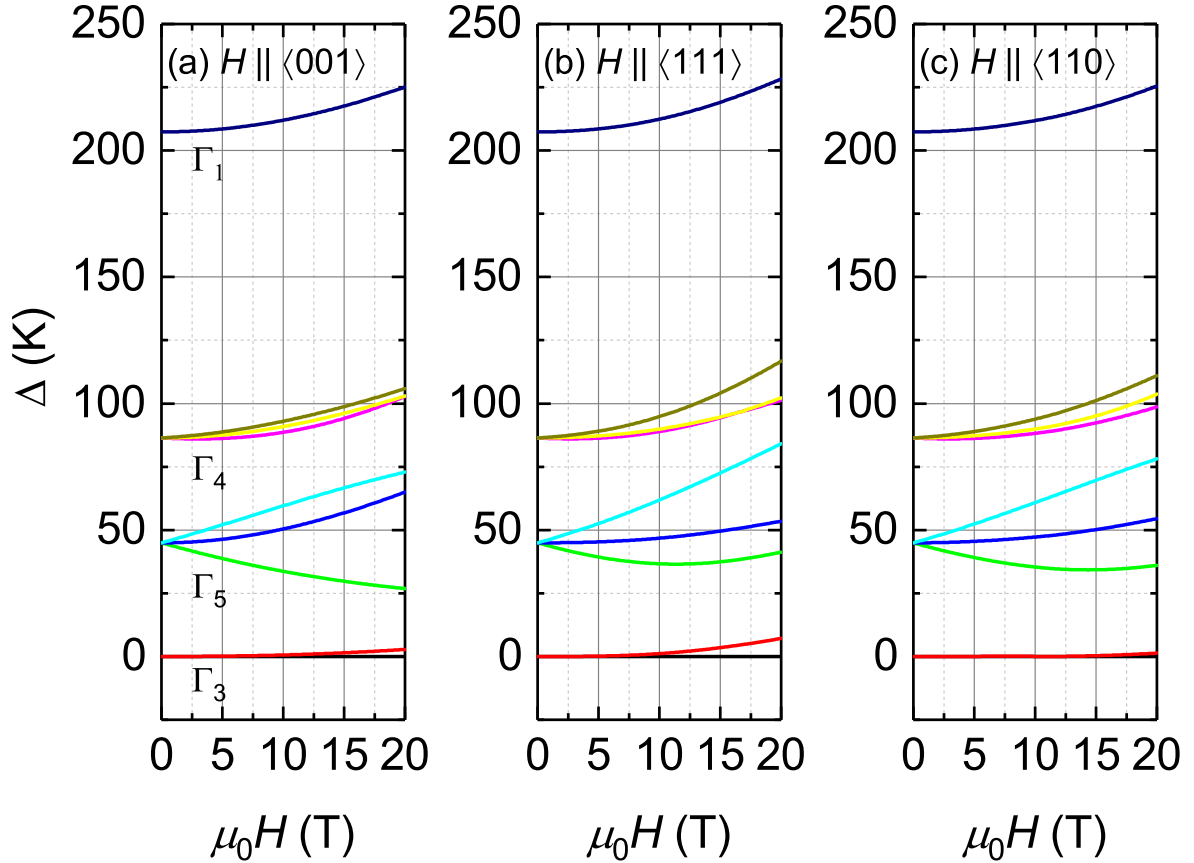


Figure 5.23: Field dependence of the CEF splitting calculated for three field directions. The CEF parameters $W = -2.87$ K and $x = -0.60$ are used for the calculation.

Shown in Fig. 5.23 is the splitting of the CEF states for three field directions calculated for $W = -2.87$ K and $x = -0.60$, that are the same values with the ones in the previous section. Under the magnetic field, the CEF states split owing to the mixing of the states. In such a case, the system is no longer isotropic and one cannot assume $K_{xx}(\omega_0) \approx K_{yy}(\omega_0) \approx K_{zz}(\omega_0)$. Then, we have to calculate $K_{xx}(\omega_0) + K_{yy}(\omega_0)$. According to Marshall and Lowde, Davidov *et al.*,

and Sugawara *et al.* [73, 74, 75, 76], $K_{xx}(\omega_0) + K_{yy}(\omega_0)$ might be expressed as:

$$K_{xx}(\omega_0) + K_{yy}(\omega_0) = k_B T \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \frac{1}{Z} \left[\sum_{\substack{i,j \\ E_i=E_j}} \frac{e^{-E_i/k_B T}}{k_B T} J_{\pm}^{ij} F_{ij}(\omega_0) + \sum_{\substack{i,j \\ E_i \neq E_j}} \frac{e^{E_i/k_B T} - e^{-E_j/k_B T}}{E_j - E_i} J_{\pm}^{ij} F_{ij}(\omega_0) \right] \quad (5.28)$$

$$J_{\pm}^{ij} = \frac{\langle i|J_{+}|j\rangle \langle j|J_{-}|i\rangle + \langle i|J_{-}|j\rangle \langle j|J_{+}|i\rangle}{2} \quad (5.29)$$

$$F_{ij}(\omega) = \frac{\Gamma_{ij}}{(\omega - \omega_{ij})^2 + \Gamma_{ij}} \quad (5.30)$$

in which $F_{ij}(\omega)$ is the distribution function of the frequency dependent $4f$ electronic fluctuation spectrum. When $4f$ electron spin fluctuations are dominated by c - f hybridization as in the present case, $F_{ij}(\omega)$ can be approximated phenomenologically to the Lorentzian form as shown in Eq. (5.30). Here, $\omega_{ij} = (E_i - E_j)/\hbar$ is the transition energy between the i th and j th eigenstates and Γ_{ij} is the HWHM of the transition linewidth between the i and j th eigenstate. Γ_{ij} can be measured by the inelastic neutron scattering. Of course, this equation can reproduce Eq (5.24) at zero field.

By using Eq. (5.28), $1/T_{1,\text{CEF}}$ can be expressed as

$$\frac{1}{T_{1,\text{CEF}}} = \frac{\gamma_n}{2} [K_{xx}(\omega_0) + K_{yy}(\omega_0)] \quad (5.31)$$

$$= \frac{\gamma_n^2}{2} k_B T \sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \left[\sum_{\substack{i,j \\ E_i=E_j}} \frac{e^{-E_i/k_B T}}{k_B T} J_{\pm}^{ij} F_{ij}(\omega_0) + \sum_{\substack{i,j \\ E_i \neq E_j}} \frac{e^{E_i/k_B T} - e^{-E_j/k_B T}}{E_j - E_i} J_{\pm}^{ij} F_{ij}(\omega_0) \right]. \quad (5.32)$$

We assume Γ_{ij} 's are i - and j -independent and $\Gamma_{ij} = \Gamma = 20$ K as used for the calculation of $K_{zz}(0)$ and take their powder average to compare with the powder averaged $1/T_1$.

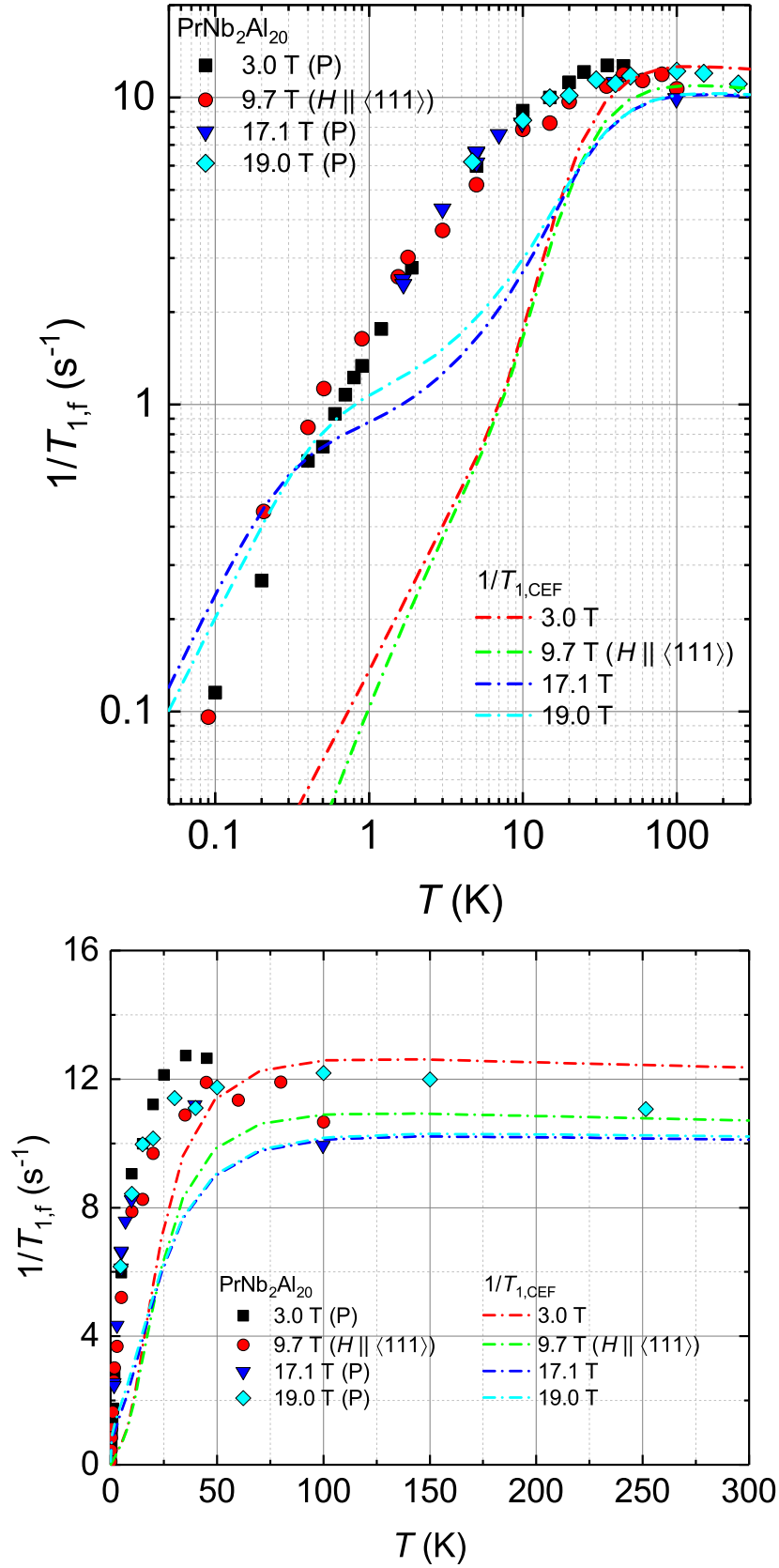


Figure 5.24: Log-log and linear plot of the temperature and field dependences of the $4f$ electronic contributions for $1/T_1$ at the Nb site in $\text{PrNb}_2\text{Al}_{20}$.

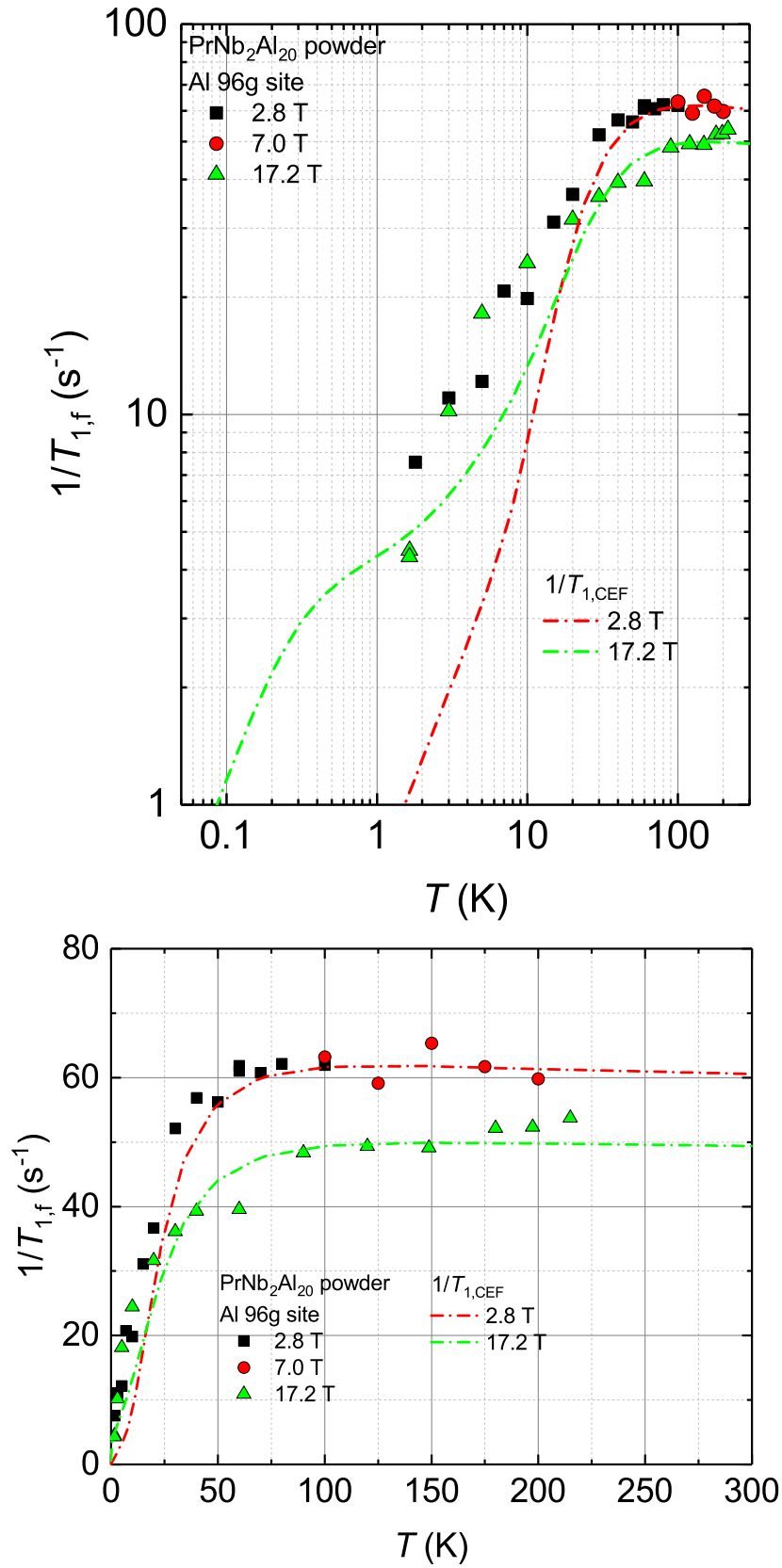


Figure 5.25: Log-log and linear plot of the temperature and field dependences of the $4f$ electronic contributions for $1/T_1$ at the Al 96g site in $\text{PrNb}_2\text{Al}_{20}$.

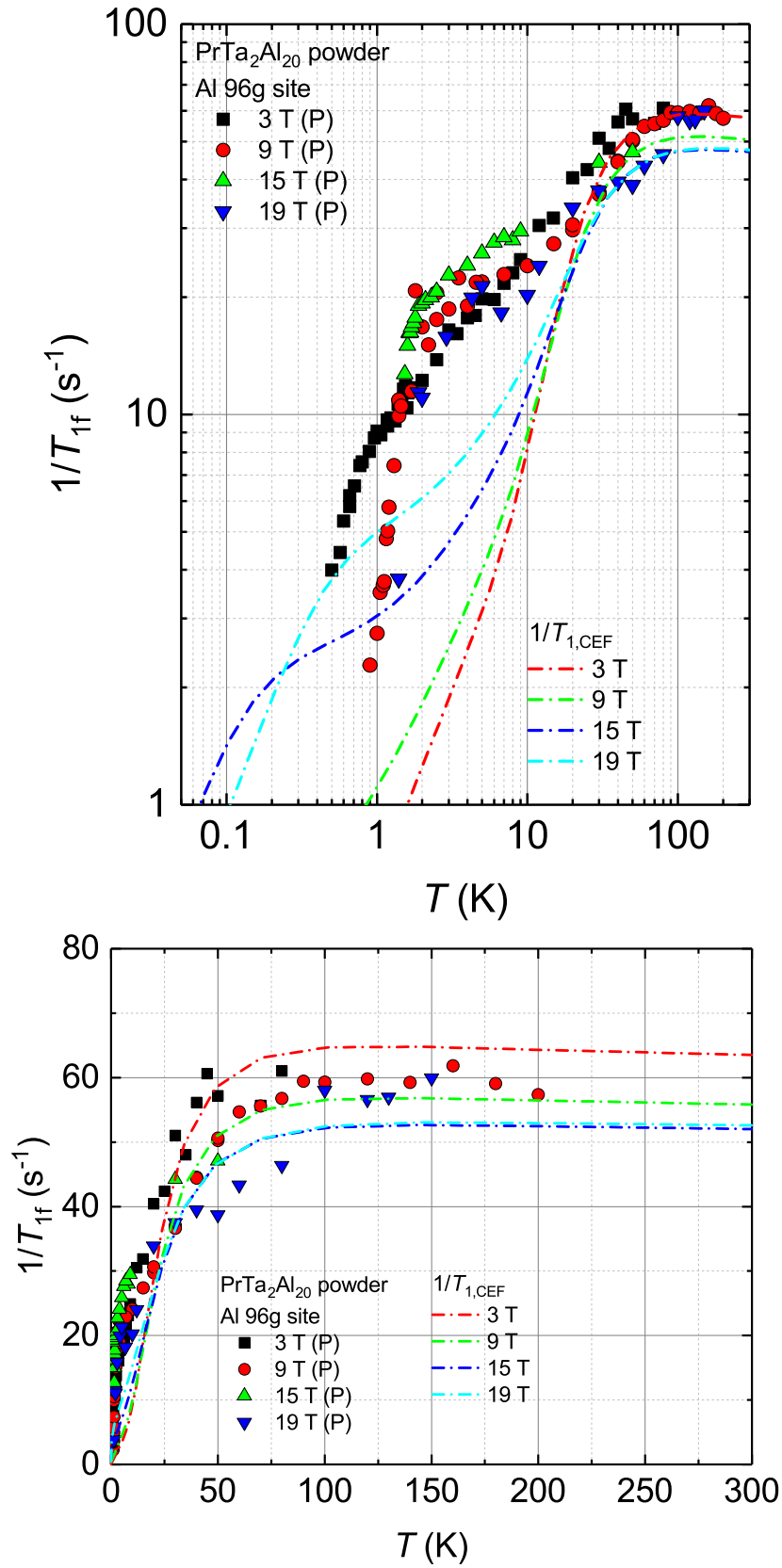


Figure 5.26: Log-log and linear plot of the temperature and field dependences of the $4f$ electronic contributions for $1/T_1$ at the Al 96g site in PrTa₂Al₂₀.

Figures 5.24–5.26 show the comparison between the experimental results and the calculation of $1/T_{1,\text{CEF}}$ under the magnetic field. The calculated $1/T_{1,\text{CEF}}$ is multiplied by 0.3–0.5 to reproduce $1/T_{1f}$ at the lowest field and highest temperature of each ligand site. The multiplication factor is fixed throughout the calculation of the field dependences. $1/T_{1,\text{CEF}}$ well explains the overall feature of $1/T_{1f}$ above 30 K for the Al 96g sites. In addition, the suppression of $1/T_{1f}$ with increasing the magnetic field can be reproduced. However, $1/T_{1f}$ below 30 K cannot be reproduced and remain relatively large values, suggesting additional fluctuations at low temperatures.

5.4.5 NMR- $1/T_1$ at low temperatures in $\text{PrNb}_2\text{Al}_{20}$

As discussed above, $\text{PrT}_2\text{Al}_{20}$ can be interpreted as a system in which 4f electrons are well localized at high temperatures. In addition, $T = \text{V, Nb}$ compounds show the relatively strong Kondo effect from the NMR viewpoints. The localized CEF model quantitatively explains the temperature and field dependences of $1/T_{1f}$ above ≈ 30 K, which is the CEF gap size between the Γ_3 ground doublet and first excited Γ_5 triplet. However, below ≈ 30 K, $1/T_{1f}$ is enhanced beyond the CEF model, suggesting the existence of fluctuations that can not be explained by the localized fluctuating 4f dipole model.

Similar enhancement of $1/T_{1f}$ has been reported in the cubic compound PrAg_2In which has the Γ_3 doublet ground state and has much smaller hybridization than $\text{PrT}_2\text{Al}_{20}$. Tanida *et al.* concluded that they detected the fluctuation of the magnetic octupole T_{xyz} by considering the bond symmetry between 4f electronic multipoles and $^{109}\text{Ag}/^{115}\text{In}$ nuclear spins [63]. In their analysis, the magnetic field effect for the CEF state was not discussed. Such a simplification is appreciable when the exchange energy of 4f electrons is much larger than the Zeeman energy. However, Tanida *et al.* present no estimation of the exchange energy. As shown in the previous section, $1/T_{1f}$ has a field-dependence at high fields. Then, to estimate the contribution of c - f hybridization and/or multipole fluctuations at low temperatures, we should subtract the CEF contribution from $1/T_{1f}$. We define $\Delta(1/T_{1f})$ as $\Delta(1/T_{1f}) \equiv 1/T_{1f} - 1/T_{1,\text{CEF}}$. $\Delta(1/T_{1f})/T$ can be regarded as $\chi''(\mathbf{q}, \omega_0)$ that comes from c - f hybridizations and/or multipole fluctuations.

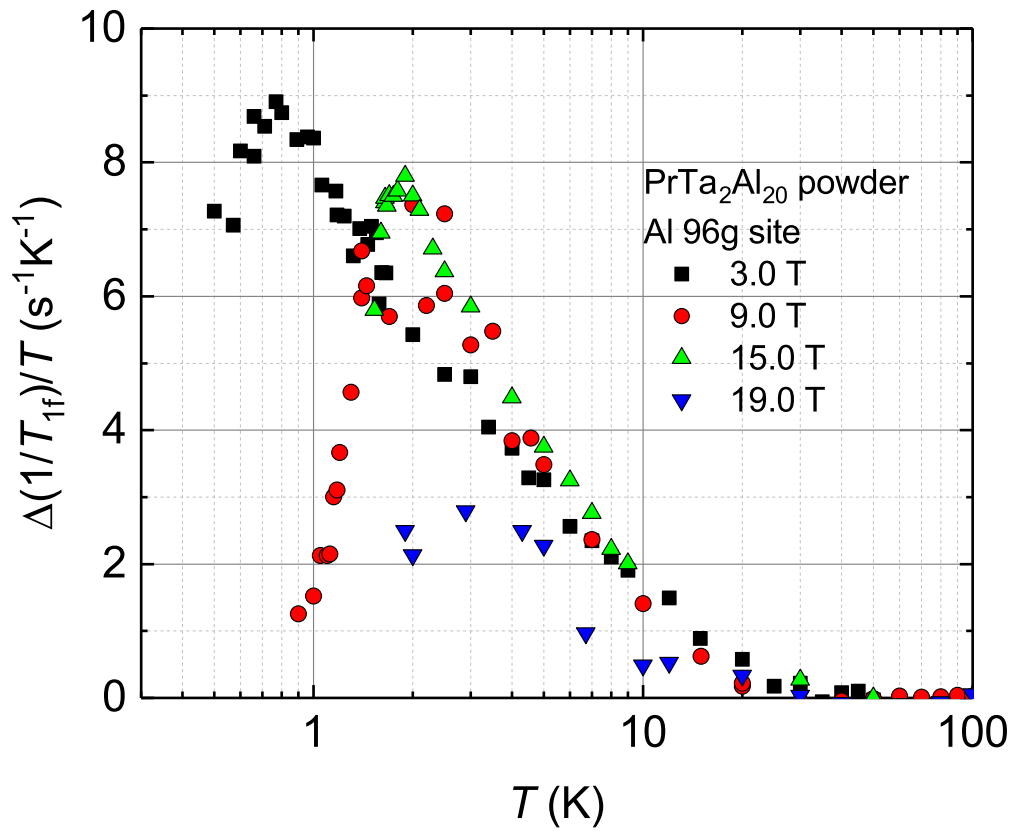
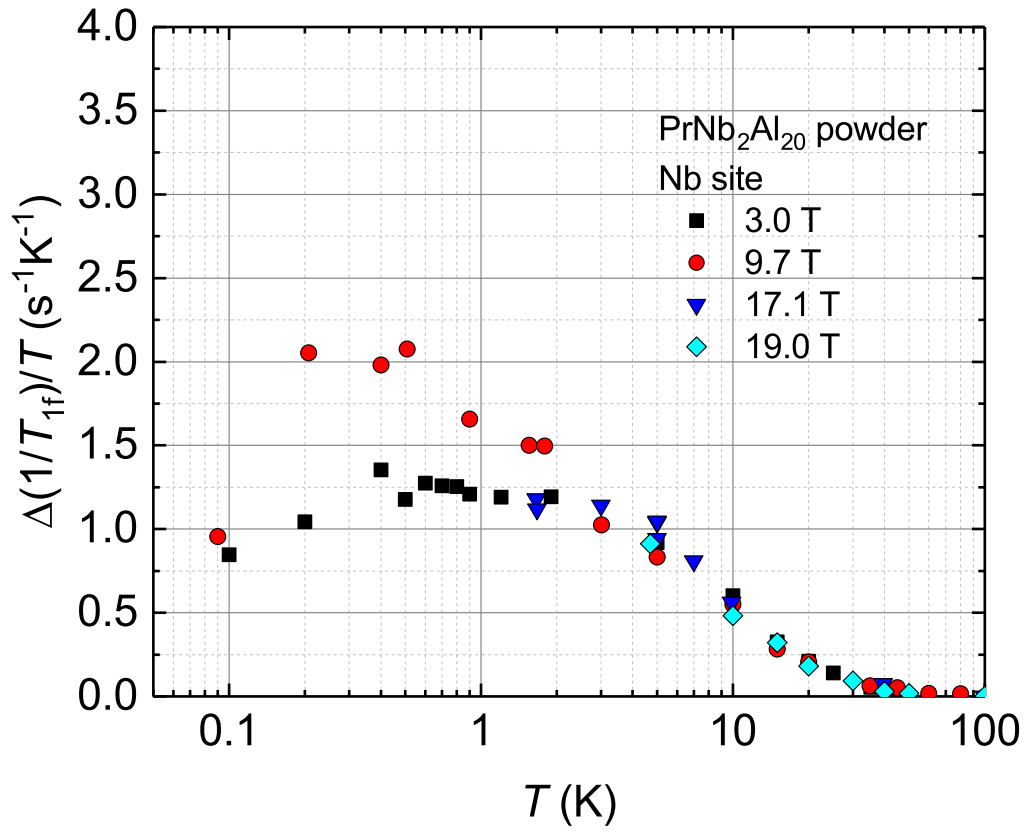


Figure 5.27: Temperature and field dependence of $\Delta(1/T_{1f})$ obtained for (upper) Nb site in PrNb₂Al₂₀ and (lower) for Al 96g site in PrTa₂Al₂₀.

Figure 5.27 shows the temperature and field dependences of $\Delta(1/T_{1f})/T$ obtained for Nb site in $\text{PrNb}_2\text{Al}_{20}$ and (lower) for Al 96g site in $\text{PrTa}_2\text{Al}_{20}$. As can be seen in the figure, $\Delta(1/T_{1f})/T$ in $T = \text{Nb}$ gradually increases below 30 K and has a broad peak at around 1 K, suggesting the development of the 4*f* electronic correlations and/or multipole fluctuations. At 3.0 and 9.7 T, the peak temperature of $\Delta(1/T_{1f})/T \approx 0.7$ K corresponds to the peak of C/T . Furthermore, this increase is almost field independent above ≈ 4 K as seen in C/T .

On the other hand, $\Delta(1/T_{1f})/T$ in $T = \text{Ta}$ shows the clear cusp at ≈ 1 K. In addition, the peak position goes higher temperatures with increasing the magnetic field. This peak temperature coincides with the bulk T_Q under the magnetic field parallel to [100] direction, suggesting the quadrupole ordering [12]. Below T_Q , $\Delta(1/T_{1f})/T$ decreases markedly, suggesting the 4*f* electronic fluctuations are suppressed owing to the opening of the gap associated with the excitation spectrum of 4*f* electrons.

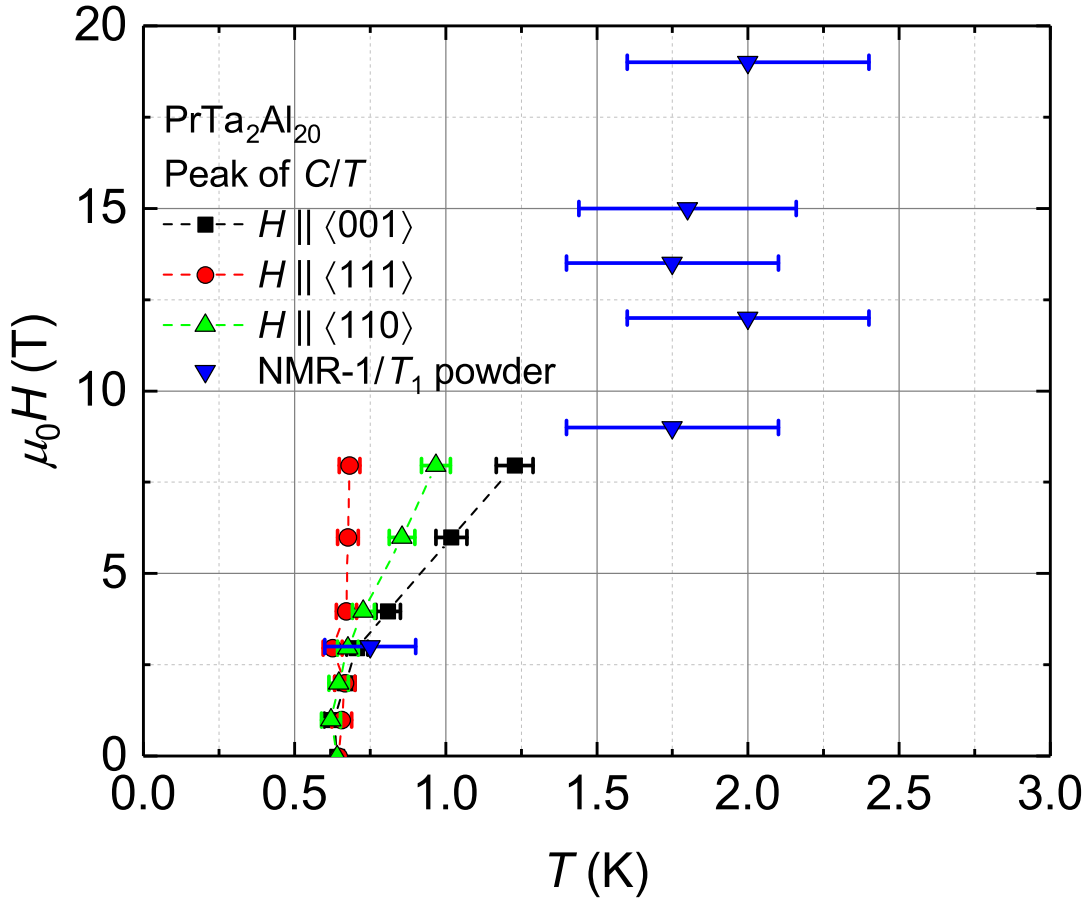


Figure 5.28: Temperature and field dependence of the peak of $\Delta(1/T_{1f})T$ obtained at Al 96g site in $\text{PrTa}_2\text{Al}_{20}$.

Figure 5.28 shows the peak temperature of $\Delta(1/T_{1f})T$ obtained at Al 96g site in $\text{PrTa}_2\text{Al}_{20}$.

The peak and sudden decrease of $\Delta(1/T_{1f})T$ remains up to 19 T, suggesting the phase transition survives such a high fields.

On the other hand, the enhancement of $\Delta(1/T_{1f})/T$ in ^{93}Nb -NMR might relate to the NFL behaviors of $\text{PrNb}_2\text{Al}_{20}$ observed in the bulk properties up to 8 T. Based on the simple localized $4f$ picture, magnetic field splits the Γ_3 doublet and the fluctuations of multipoles are expected to be suppressed. Indeed, in $\text{PrIr}_2\text{Zn}_{20}$ at high field above 6 T and below 1 K, the ground state of $4f$ electrons becomes the CEF singlet state and the anomalous metallic behavior disappears [37]. This is completely different from the case of $\text{PrNb}_2\text{Al}_{20}$, which shows a field insensitive NFL state.

The enhancement $\Delta(1/T_{1f})/T$ up to 19 T suggests that $\text{PrNb}_2\text{Al}_{20}$ has strong c - f hybridizations and/or multipole fluctuations, and such fluctuations contribute to the NFL behavior observed in the bulk properties.

In the next section, we discuss about the ground state of $4f$ electrons in $\text{PrNb}_2\text{Al}_{20}$ from the NQR viewpoint.

5.5 ^{93}Nb -NQR measurements and the anomalous electronic states at low temperatures in $\text{PrNb}_2\text{Al}_{20}$

In this section, we discuss about the electronic states in $\text{PrNb}_2\text{Al}_{20}$ at low temperatures at zero magnetic field by using ^{93}Nb -NQR.

5.5.1 ^{93}Nb -NQR spectra

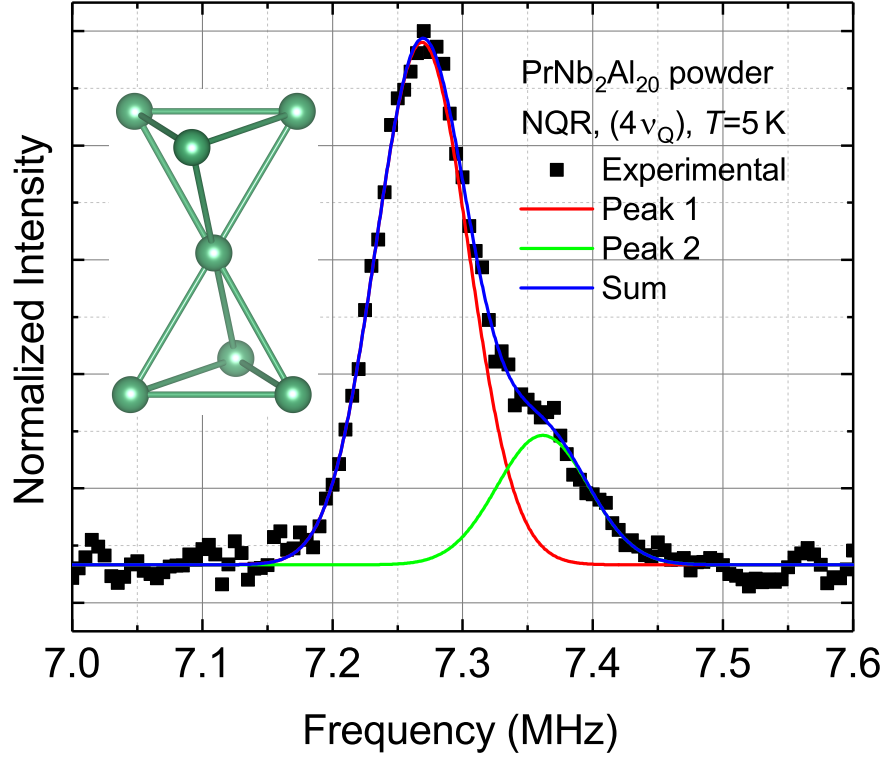


Figure 5.29: ^{93}Nb -NQR $4\nu_Q$ line obtained at 5 K. The red solid, blue dashed, and green dotted lines represent the result of the fitting assuming two Gaussian peaks (1 and 2). The inset is a schematic picture of the first-nearest-neighboring Nb sites around a specific Nb site.

Shown in Fig. 5.29 is the ^{93}Nb -NQR spectrum measured at $4\nu_Q \approx 7.26 \text{ MHz}$ and 5 K. As clearly seen in the figure, the spectrum has asymmetrical line shape, with a shoulder at higher frequencies. Such a shoulder is commonly observed for other transition lines and this tendency is more prominent in the $4\nu_Q$ transition. Furthermore, the asymmetrical line is also observed for the single crystal sample. Therefore, this shoulder is not attributed to strains introduced by grinding. The observed spectrum is roughly reproduced by the superposition of a peak at around 7.26 MHz (peak 1) and a peak at around 7.36 MHz (peak 2). The red solid line in Fig. 5.29 is the result of a simulation assuming two Gaussian lines (the blue dashed and

the green dotted ones). The ratio of the integrated intensity of the peak 1 to the peak 2 is about 0.8 : 0.2 and is temperature independent. Since the Nb occupancy is about 0.97 in the present sample [51], we calculate the influence of the Nb defect. As shown in the inset of Fig. 5.29, there are six first-nearest-neighboring Nb atoms around a specific Nb site. Here we assume that peak 1 originates from the Nb atoms where the first-nearest-neighboring Nb atoms are fully occupied, whereas peak 2 originates from the Nb atoms where at least one of the first-nearest-neighboring Nb atoms is absent. Then, the respective probabilities for peak 1 and peak 2 are roughly estimated as $P_1(x) \approx x^6 \approx 0.83$ and $P_2(x) \approx 1 - P_1(x) \approx 0.17$ using the binomial distribution with the Nb occupancy $x = 0.97$. The ratio $P_1 : P_2$ is very close to the observed intensity ratio. Thus, the shoulder structure is attributed to the effect of 3% Nb defects.

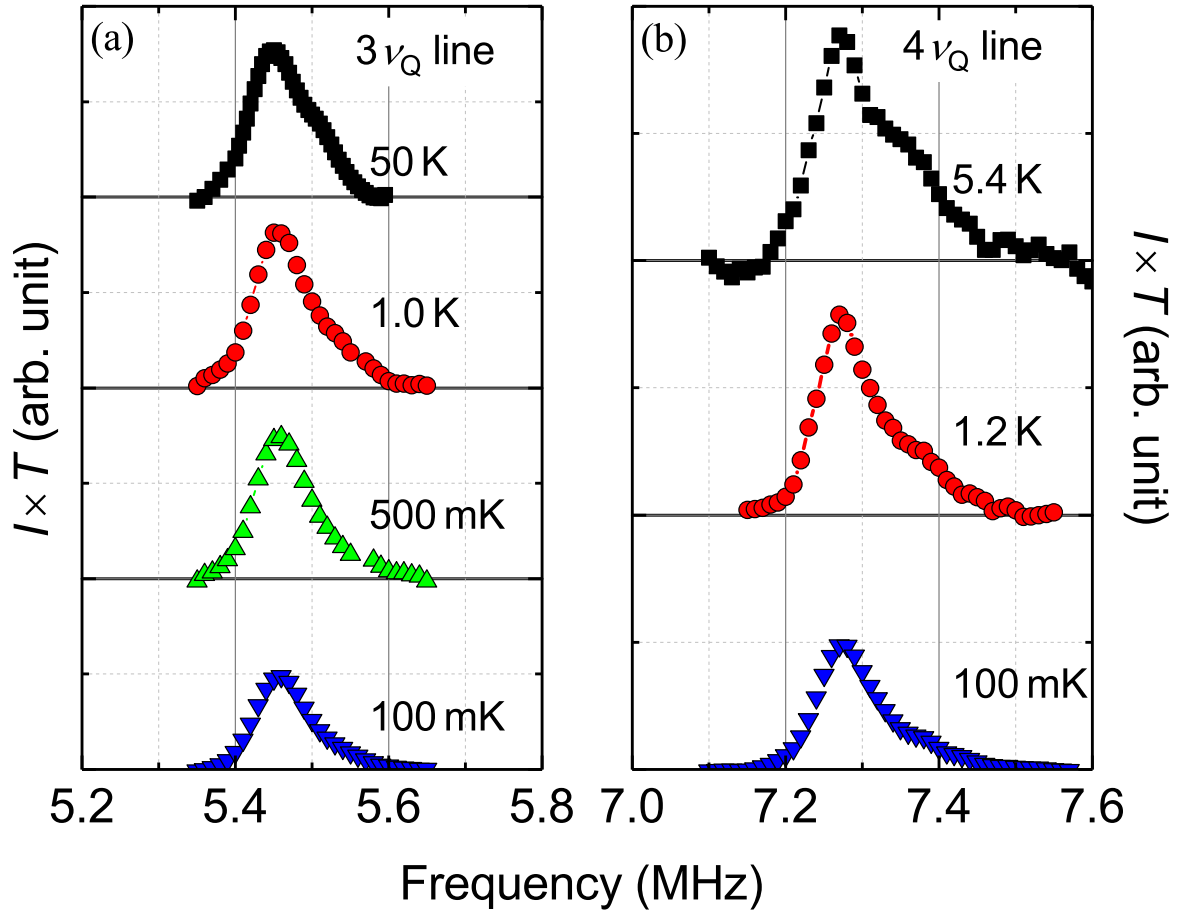


Figure 5.30: Temperature dependences of (a) ^{93}Nb -NQR $3\nu_Q$ line and (b) $4\nu_Q$ line. Intensities are corrected by the Boltzmann factor.

Figures 5.30(a,b) display the temperature dependences of ^{93}Nb -NQR spectra at resonance frequencies of $3\nu_Q \approx 5.45$ MHz and $4\nu_Q$. Here, the intensity I of each spectrum was corrected

by the Boltzmann factor, i.e., the product of intensity and temperature $I \times T$ is shown. The linewidth for $4\nu_Q$ is broader than that of $3\nu_Q$ and is proportional to ν_Q . This result indicates that the linewidth is dominated by the distribution of the EFG at Nb sites. The line shape of the ^{93}Nb -NQR spectra does not change down to 0.1 K. In order to determine whether or not the Nb site is a magnetically symmetric site in the spin structure, the magnetic hyperfine form factor $F(\mathbf{q})$ at the Nb site was calculated by considering the nearest neighboring Pr atoms. Taking the origin at the Nb atom, there are six nearest neighbor Pr atoms. The Fourier expansion of the Pr spin, $\mathbf{J}_i$ at the i th site is expressed as $\mathbf{J}_i = \sum_{\mathbf{q}} \mathbf{J}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}_i)$, where $\mathbf{r}_i$'s are the position of the nearest neighboring Pr sites. Thus, in general, we have $F(\mathbf{q}) = |\sum_i \exp(i\mathbf{q} \cdot \mathbf{r}_i)|^2$. Owing to the diamond structure of the Pr site, $F(\mathbf{q})$ at the Nb site is obtained as

$$F(\mathbf{q}) = 4 \left[\cos \left(\frac{-3q_x + q_y + q_z}{8} \right) + \text{c.p.} \right]^2, \quad (5.33)$$

where $\mathbf{q} = (q_x, q_y, q_z)$ is the magnetic wave vector, and c.p. denotes cyclic permutations of q_x , q_y , and q_z . It appears that the internal field at the Nb site cannot be canceled out for any antiferromagnetic wave vector of the diamond structure. Thus, the present ^{93}Nb -NQR measurements fail to detect any signature of a long-range magnetic dipole order down to 0.1 K, providing microscopic evidence for the absence of a static magnetic dipole ordering. However, the spectral intensity of each line decreases with decreasing temperature. Note that $I \times T$ is in general proportional to the number of observed nuclei and is constant against temperature. Later we discuss about the decrease of $I \times T$.

5.5.2 ^{93}Nb -NQR longitudinal relaxation rate $1/T_1$ and the enhanced ^{141}Pr nuclear magnetism

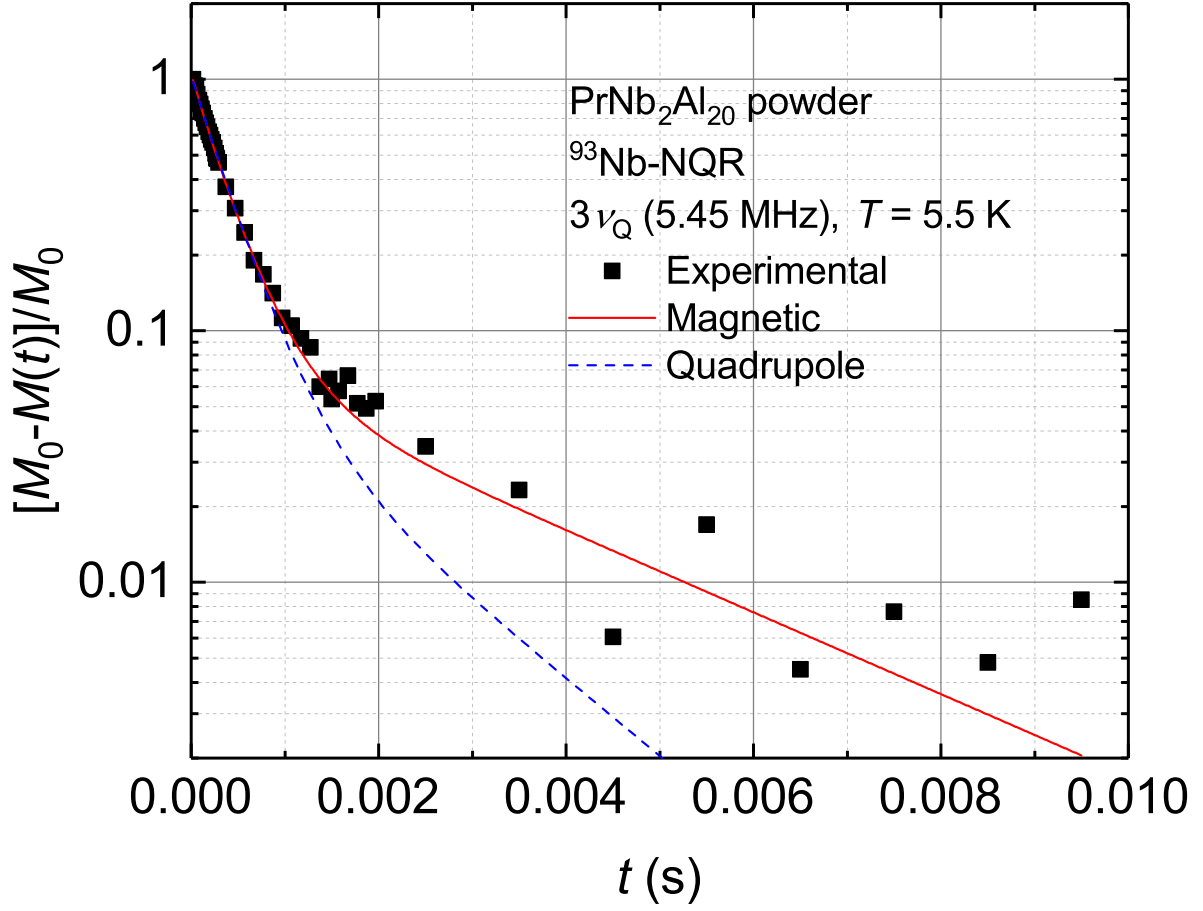


Figure 5.31: Typical relaxation curve obtained for the $3\nu_Q$ line at 5.5 K. The red solid line indicates the relaxation curve assuming a pure magnetic relaxation process and the blue dashed line indicates that assuming a pure quadrupole relaxation process.

The ^{93}Nb -NQR nuclear longitudinal relaxation rate $1/T_1$ was measured at the $2\nu_Q \approx 3.65$ MHz, $3\nu_Q$, and $4\nu_Q$ lines. Figure 5.31 shows a typical NQR longitudinal relaxation curve obtained for the $3\nu_Q$ line at 5.5 K. While $1/T_1$ in NMR is dominated by magnetic relaxation especially at high temperatures, the NQR T_1 process in PrNb₂Al₂₀ is not simple. That is, $4f$ electric quadrupole fluctuation as well as magnetic dipole/octupole fluctuation causes the relaxation because the Γ_3 state has two quadrupoles and one octupole and the Γ_4 and Γ_5 states have dipole and five quadrupoles at zero fields.

Since electric quadrupoles may contribute to the nuclear relaxation at zero field, we calculated the relaxation function of the magnetic/electric origin and fitted the experimental result

to check the origin of the NQR relaxation process. As discussed in §5.3.2, the time-dependent nuclear magnetization, $M(t)$, after a single $\pi/2$ pulse for a ^{93}Nb -NQR transition line is obtained as

$$M(t) = M_0 \left[1 - \sum_{i=1}^4 \alpha_i \exp\left(-\frac{\beta_i t}{T_1}\right) \right]. \quad (5.34)$$

For a $3\nu_Q$ line and a pure magnetic relaxation process, $M(t)$ can be expressed as

$$\frac{M_\infty - M(t)}{M_0} = \frac{3}{44}e^{-3t/T_1} + \frac{5}{572}e^{-10t/T_1} + \frac{147}{220}e^{-21t/T_1} + \frac{729}{2860}e^{-36t/T_1}. \quad (5.35)$$

On the other hand, for a $3\nu_Q$ line and a pure quadrupole relaxation process assuming $W_1 = W_2$, $M(t)$ is obtained to be

$$\frac{M_\infty - M(t)}{M_0} = \frac{3}{44}e^{-23t/48T_1} + \frac{5}{572}e^{-65t/48T_1} + \frac{729}{2860}e^{-13t/8T_1} + \frac{147}{220}e^{-49t/24T_1}. \quad (5.36)$$

As shown in Fig. 5.31, the relaxation curve for the magnetic relaxation, which fits the data over two orders of magnitude, is fitted better than that for the quadrupole relaxation. This result strongly indicates that the ^{93}Nb -NQR relaxation is dominated by a magnetic fluctuation.

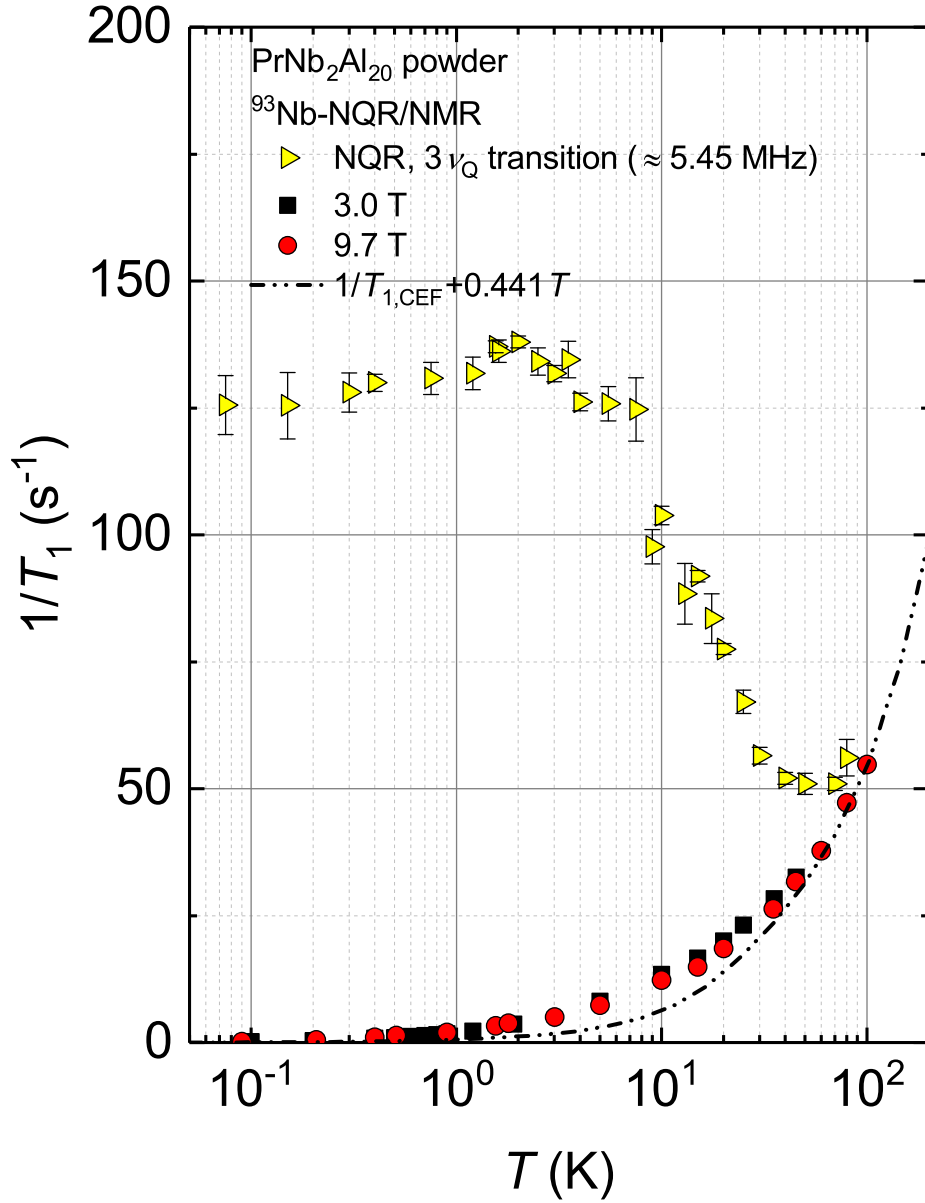


Figure 5.32: Temperature dependence of ⁹³Nb-NQR/NMR $1/T_1$ measured at NQR- $3\nu_Q$ transition, 3.0 T, and 9.7 T. A dash-dotted line is the calculated $1/T_1$ by the localized CEF model. Details are described in the text.

Figure 5.32 displays the temperature dependence of ⁹³Nb-NQR $1/T_1$ measured at $3\nu_Q$ transition and NMR $1/T_1$ at 3.0 and 9.7 T discussed previously. Below 30 K, $1/T_1$ increases rapidly with decreasing temperatures and saturates around 5 K. The increase in $1/T_1$ suggests that magnetic correlations evolve with decreasing temperature. The behavior of $1/T_1 = \text{const.}$ below 5 K down to 0.075 K indicates that local moments still fluctuate at low temperatures. No anomaly was found in the temperature dependence of $1/T_1$ below 5 K, evidencing the absence

of a magnetic dipole phase transition down to 0.075 K at zero external field. This behavior is considerably different from that of ^{93}Nb - and ^{27}Al -NMR $1/T_1$ for $\text{PrT}_2\text{Al}_{20}$ discussed previously.

Next, we discuss the origin of the longitudinal relaxation process in $\text{PrNb}_2\text{Al}_{20}$ at low temperatures. As discussed in §3, the magnetic relaxation process basically occurs through the spin-flip process between states $|-1/2\rangle$ and $|+1/2\rangle$ of the conduction electrons through c - f exchange interactions such as $J_{\text{ex}}\mathbf{s} \cdot \mathbf{J}$, where J_{ex} , $\mathbf{s}$, and $\mathbf{J}$ are the exchange coupling constant, conduction electron spin, and f electron spin associated with the CEF ground state, respectively. In this case, the nuclear longitudinal relaxation at a ligand site occurs through $\mathbf{I} \cdot \tilde{\mathbf{A}}_{\text{tr}} \cdot \mathbf{s}$, where $\tilde{\mathbf{A}}_{\text{tr}}$ is the transferred hyperfine interaction tensor and $\mathbf{s}$ is related to $\mathbf{J}$. Thus, nuclear spin $\mathbf{I}$ flips accompany the spin-flop process of $\mathbf{J}$. Since the Γ_3 ground state is nonmagnetic, only the low-energy spin fluctuations of magnetic Γ_4 and Γ_5 excited states contribute to the dependence of the relaxation process on the temperature. The high-energy Van Vleck susceptibilities do not contribute to the relaxation process.

For the CEF scheme of Γ_3 (0 K)– Γ_5 (44.8 K)– Γ_4 (86.1 K)– Γ_1 (206.6 K) obtained from the inelastic neutron scattering as described above and the magnetic relaxation process, $1/T_1$ is expected to decrease markedly far below ≈ 50 K because the depopulation of the excited magnetic Γ_5 and Γ_4 triplets as discussed in the previous section. The black dashed-dotted line is the calculated $1/T_1$ by adding $1/T_{1,\text{CEF}}$ using above CEF scheme and the conduction electron contribution $1/T_1 = 0.441T$. As clearly seen in the figure, the simple CEF model cannot explain the experimental data. On the other hand, the fluctuation of the T_{xyz} octupole moment is a possible origin of the magnetic relaxation for the Γ_3 CEF ground state.

The origin of the magnetic relaxation process exists, however, other than the fluctuation of the T_{xyz} octupole moment. Several Pr-based compounds having a nonmagnetic ground state are known to be Van Vleck paramagnets, in which the hyperfine interaction between $4f$ electron spins and a nuclear spin in each atom enhances the nuclear moment by a factor $1 + K \approx 6$ –20 from the bare value. Here, $K = {}^{141}a_{\text{hf}}\chi_{\text{VV}}$ is the ${}^{141}\text{Pr}$ Knight shift, where ${}^{141}a_{\text{hf}} \approx 187.7$ mol/emu is the intra-atomic hyperfine coupling constant between ${}^{141}\text{Pr}$ nuclei and $4f$ electrons [77], $\chi_{\text{VV}} \approx 0.065$ emu/mol is the $4f$ electronic Van Vleck susceptibility at 1 K. By substituting the above values, we can estimate $1 + K \approx 12$. In this case, $1/T_1$ is enhanced through the slow fluctuation arising from the hyperfine-enhanced nuclear moment at low temperatures and low frequencies [78]. Such contributions have been detected in PrAg_2In [79], $\text{PrFe}_4\text{P}_{12}$ [66], $\text{PrOs}_4\text{Sb}_{12}$ [62, 80], and $\text{PrT}_2\text{Al}_{20}$ ($T = \text{Ti, V}$) [81, 82].

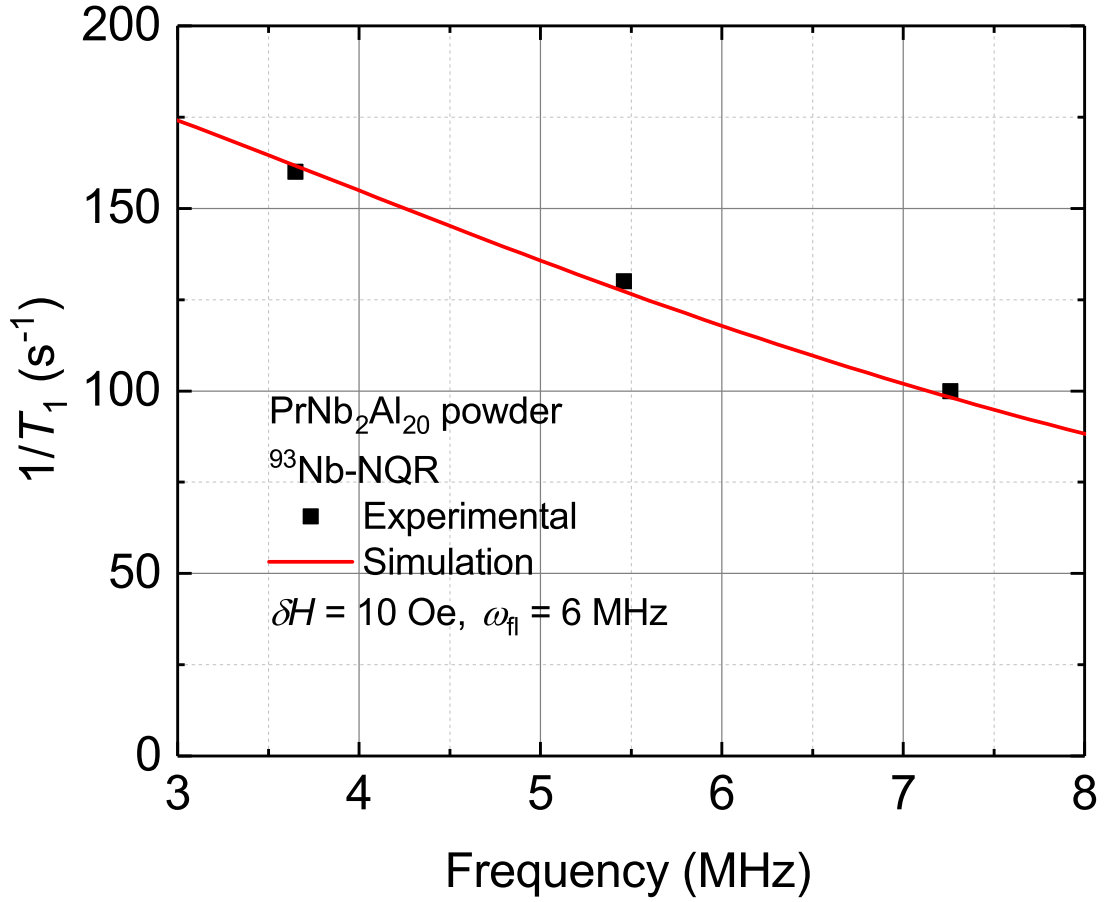


Figure 5.33: Frequency dependence of $1/T_1$ measured at 5 K. The red solid line represents the calculated $1/T_1$ based on the cross-relaxation model described in the text.

In order to determine whether the fluctuation due to the hyperfine-enhanced nuclear moment contributes to the relaxation rate, the frequency dependence of ^{93}Nb -NQR $1/T_1$ was measured for the lines corresponding to $2\nu_Q$, $3\nu_Q$, and $4\nu_Q$ transitions and the result is shown in Fig. 5.33. Since the quadrupole relaxation curves for $2\nu_Q$ and $4\nu_Q$ are worse fitting than the magnetic relaxation curves as is the case of $3\nu_Q$, we dealt with the magnetic relaxation. Here, the relaxation curve for $2\nu_Q$ is

$$\frac{M_{\infty} - M(t)}{M_0} = \frac{1}{33}e^{-3t/T_1} + \frac{20}{143}e^{-10t/T_1} + \frac{4}{165}e^{-21t/T_1} + \frac{576}{715}e^{-36t/T_1}, \quad (5.37)$$

and for $3\nu_Q$ is

$$\frac{M_{\infty} - M(t)}{M_0} = \frac{4}{33}e^{-3t/T_1} + \frac{80}{143}e^{-10t/T_1} + \frac{49}{165}e^{-21t/T_1} + \frac{16}{715}e^{-36t/T_1}. \quad (5.38)$$

As clearly seen in Fig. 5.33, the relaxation rate shows a strong frequency dependence.

Then, the frequency dependence of $1/T_1$ was analyzed by the cross-relaxation process between ^{93}Nb nuclear magnetic moment and enhanced ^{141}Pr moment as discussed in Refs. [62, 66, 79, 80, 81, 82].

$$\frac{1}{T_1} = 2\gamma_n^2 \delta h^2 \frac{\omega_{\text{fl}}}{\omega_{\text{fl}}^2 + \omega_0^2}, \quad (5.39)$$

where δh is the magnitude of the fluctuating internal fields, ω_{fl} is the characteristic frequency of fluctuations, and ω_0 is the NQR resonance frequency. As clearly seen in Eq. (5.39), $1/T_1$ depends on ω_0 . δh is expressed as:

$$\delta h = \sqrt{\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 (1 + K) \frac{g_n \mu_n}{g_J \mu_B}}, \quad (5.40)$$

where $g_n = 1.71$ is the ^{141}Pr nuclear g -factor, μ_N is the nuclear magneton. We can estimate δh by using $\sum_{\mathbf{q}} |A_{\mathbf{q}}|^2 \approx 660^2 \text{ Oe}^2$ and $1 + K \approx 12$ as estimated above to be $\delta h \approx 10 \text{ Oe}$. The red solid line in Fig. 5.33 is the result of the calculation using $\delta h = 10 \text{ Oe}$ and $\omega_{\text{fl}}/2\pi = 6 \text{ MHz}$. The agreement between experiment and calculation is quite satisfactory and the obtained values are almost consistent with those in other Pr-based compounds [62, 66, 79, 80, 81, 82]. Thus, the frequency dependence of $1/T_1$ is ascribed to be related to the fluctuation of an enhanced ^{141}Pr nuclear moment in $\text{PrNb}_2\text{Al}_{20}$. Therefore, this result provides strong support to the fact that the nonmagnetic Γ_3 CEF ground state is realized in $\text{PrNb}_2\text{Al}_{20}$.

5.5.3 Low temperature behaviors in NQR/NMR

In this section we discuss the possibility of a quadrupole or higher order multipole ordering. At low temperatures, the Γ_3 doublet ground state in the T_d symmetry possesses O_{20} and O_{22} type quadrupole moments and a T_{xyz} type octupole moment. In general, the nuclear electric quadrupole moment and the nuclear magnetic moment of a ligand nucleus can couple with $4f$ -derived multipole moments with the same time-reversal symmetry [63, 83, 84]. For example, the local bond symmetry of the Pr-Nb bond for the Nb nucleus at $(1/2, 1/2, 1/2)$ and a Pr ion at $(1/4, 1/4, 1/4)$ is C_s with respect to the $[1\bar{1}0]$ mirror plane. Therefore, O_{20} and O_{22} can couple with the Nb nuclear quadrupole moment and T_{xyz} can couple with the Nb nuclear magnetic moment. The invariant form of the quadrupole and hyperfine coupling of the Nb nucleus and

the Pr ion can be expressed as [63]:

$$\begin{aligned} \mathcal{H}_{\text{Nb-Pr}} = & -\gamma_n \hbar \frac{1}{\sqrt{3}} (I_x + I_y + I_z) C_{\text{Nb}} T_{xyz} \\ & + \frac{eQ}{4I(2I-1)} \left[\left(3I_z^2 - I(I+1) \right) P_{\text{Nb}}^1 O_{20} + \left(I_x^2 - I_y^2 \right) P_{\text{Nb}}^2 O_{22} \right], \end{aligned} \quad (5.41)$$

where C_{Nb} is the transferred hyperfine coupling constant associated with the coupling between the T_{xyz} moment and the Nb nuclear magnetic moment, and P_{Nb}^1 and P_{Nb}^2 are the transferred quadrupole coupling constants with the coupling between the Nb nuclear quadrupole moment and the corresponding components of the EFG tensor at the Nb site [84]. Note that the EFG tensors at the Nb site reflect the quadrupole moments of the Pr Γ_3 state via hybridization. In the para quadrupole state, neither O_{20} nor O_{22} has a nonzero thermal average. In the same manner, the thermal average of the octupole moment is zero in the para octupole state. If one of these multipole moments has a finite thermal average, the system should undergo a transition into either a quadrupole or an octupole ordered state. In such a state, the ^{93}Nb -NQR spectrum is expected, in principle, to change its line profile. Unfortunately, because we have no way of knowing the magnitude of the transferred multipole coupling constants at the present stage, it is difficult to conclude the absence of the quadrupole or octupole order only from the present analyses. Nevertheless, as we discussed above, the experimental findings of $1/T_1 \approx \text{const.}$ below 5 K down to 0.075 K together with the behaviors of bulk measurements [11, 12], a static long-range quadrupole or octupole ordered state is unlikely to occur down to 0.075 K.

As the last part of this section, we discuss the decrease of the NQR signal intensity and the fluctuations of multipoles.

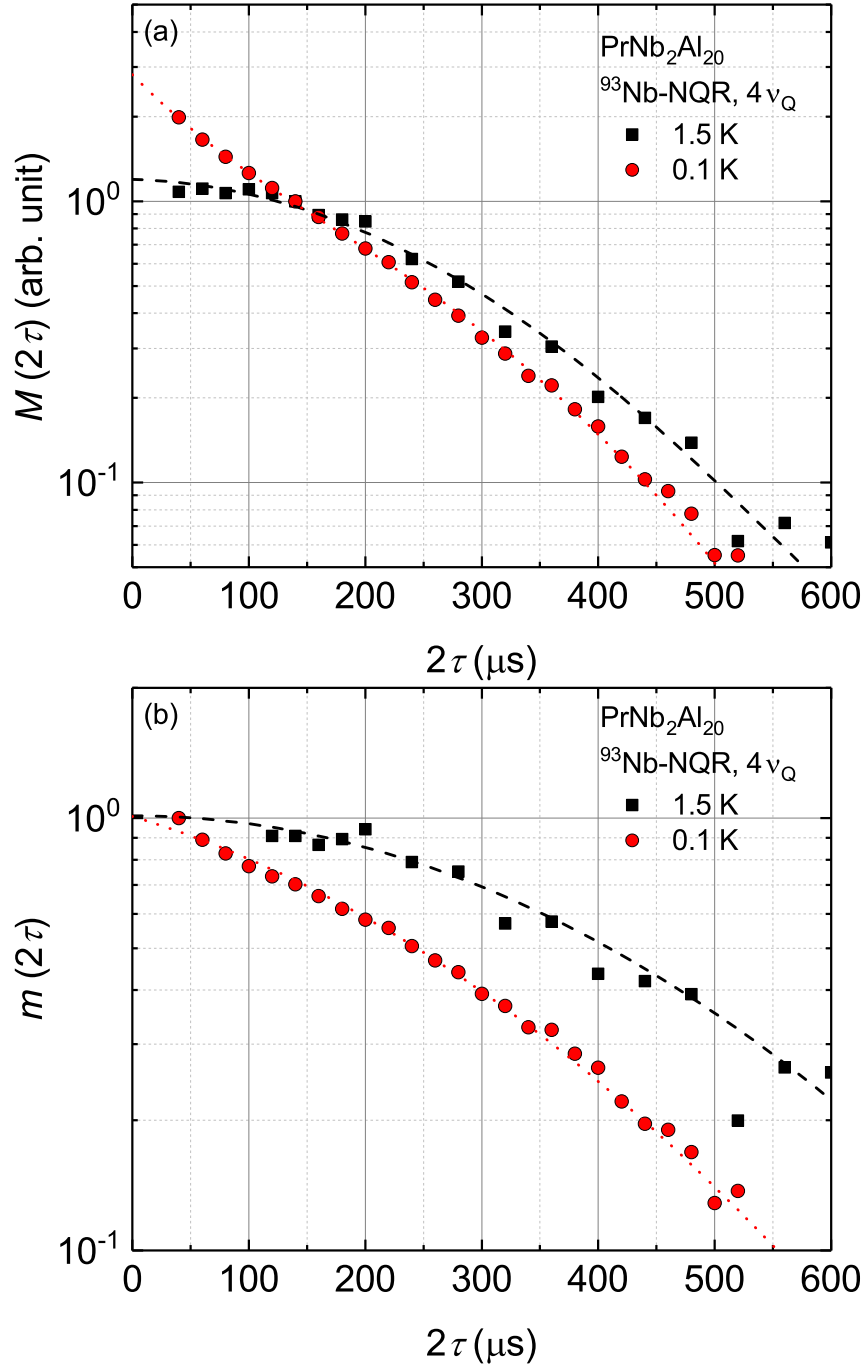


Figure 5.34: (a) Temperature dependence of the ^{93}Nb -NQR spin-echo decay curve measured at the $4\nu_Q$ line and at 1.5 K and 0.1 K. Intensities are normalized by that at $2\tau = 140 \mu\text{s}$. The black dashed and red dotted lines represent the calculated decay curves assuming Gaussian times Lorentzian decay described in the text. (b) Temperature dependence of the intrinsic spin-echo decay process. The contribution of the isotropic spin lattice relaxation, $1/T_{2R} = (I + 1/2)^2/T_1 = 3300 \text{ s}^{-1}$, is subtracted. The black dashed and red dotted lines represent the calculated decay curves assuming Gaussian and Gaussian times Lorentzian decay, respectively. Details are described in the text.

Figure 5.34(a) shows typical spin-echo decay curves measured at 1.5 K and 0.1 K. Here the spin-echo decay curve was obtained by recording the spin-echo amplitude $M(2\tau)$ of the $^{93}\text{Nb-}4\nu_Q$ line as a function of the time interval τ between the first exciting and second refocusing pulses. At high temperatures, a Gaussian decay component is dominant. With decreasing temperature, a Lorentzian decay component appears to evolve below 0.5 K and the curve cannot be fitted by simple Gaussian decay.

As described above, $1/T_1$ remains almost constant with a relatively large value at low temperatures below 5 K. Thus, the T_1 process should be taken into consideration to discuss the spin-echo decay rate. The observed spin echo-decay curve is expressed as $M(\tau) = M_0 \exp(-2\tau/T_{2R}) m(2\tau)$ with the T_1 process of $1/T_{2R} = (I + 1/2)^2 T_1$ assuming the isotropic longitudinal relaxation [85, 86]. Here $m(2\tau)$ is the intrinsic spin-spin relaxation process and we adopted the Gaussian function of $m(2\tau) = \exp\left[-(2\tau/T_{2G})^2\right]$ above 0.5 K. On the other hand, below 0.5 K, the data cannot be fitted by a simple Gaussian function. Then we tentatively fitted the data by the Gaussian times Lorentzian form of $m(2\tau) = \exp\left[-(2\tau/T_{2G})^2\right]$. The dotted lines in Fig. 5.34 are the best fits to the data with $1/T_{2R} = 1/3300 \text{ s}^{-1}$.

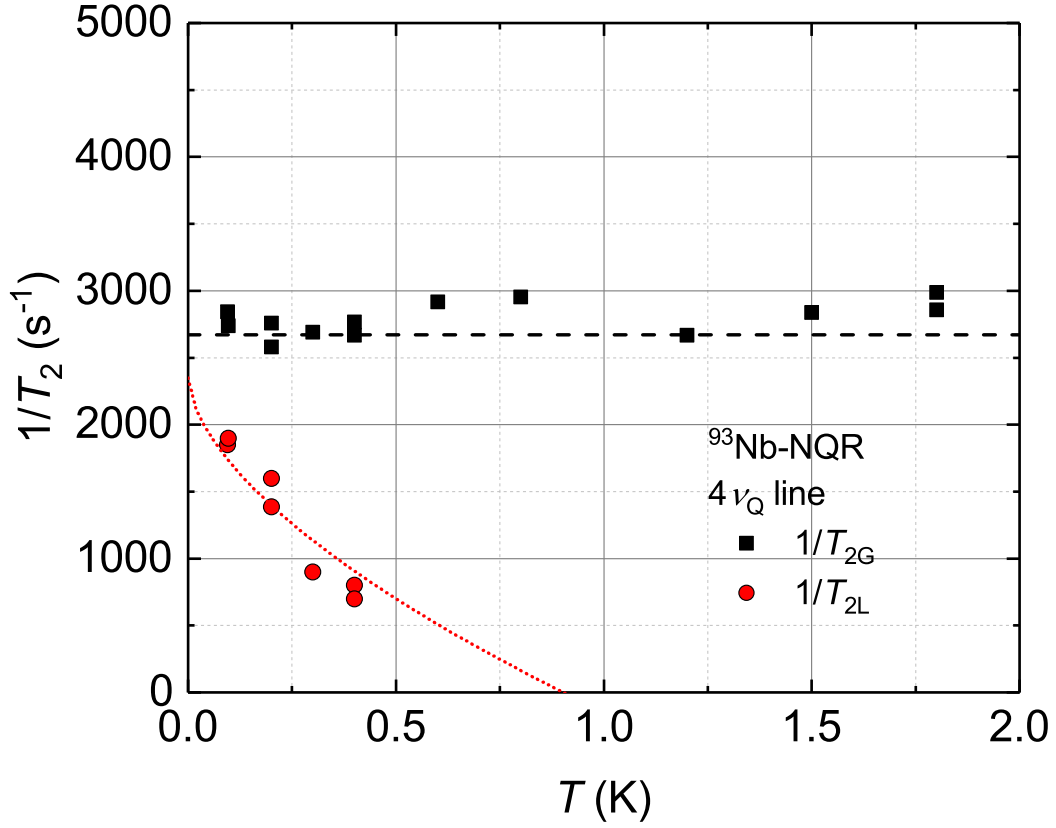


Figure 5.35: Temperature dependences of the spin-echo decay rates $1/T_2$. The black dashed and red dotted lines display the calculated Gaussian component and a guide for the eyes showing the development of the Lorentzian component, respectively.

The temperature dependences of $1/T_{2G}$ and $1/T_{2L}$ are shown in Fig. 5.35. $1/T_{2G}$ has a constant value of $\approx 3000 \text{ s}^{-1}$.

In general, the Gaussian relaxation process arises from direct nuclear dipole-dipole interactions, which form a homogeneous internal field at atomic sites. Assuming the powder average, the Gaussian spin-echo decay rate for like (Nb) spins I is given by

$$\frac{1}{T_{2G}^{\text{like}}} = \frac{1}{2\pi} \sqrt{\frac{3}{5} \gamma_{\text{Nb}}^4 \hbar^2 I(I+1) \sum_k \frac{1}{r_k^6}}, \quad (5.42)$$

where r_k is the distance between two Nb nuclei. For unlike spins, we have

$$\frac{1}{T_{2G}^{\text{unlike}}} = \frac{1}{2\pi} \sqrt{\frac{4}{15} \gamma_{\text{Nb}}^2 \gamma_S \hbar^2 S(S+1) \sum_{k'} \frac{1}{r_{k'}^6}}, \quad (5.43)$$

where S is the nuclear spin of the other species, γ_S is its gyromagnetic ratio, and $r_{k'}$ is the

distance between a Nb nucleus and an unlike nucleus [39, 87].

By performing the lattice sum for both k and k' , the Gaussian spin–spin relaxation rates for Pr, Nb, Al 16c, Al 48f, and Al 96g atoms were estimated to be $\approx 160, 510, 230, 1630$, and 1300 s^{-1} , respectively. By adding all the contributions, $1/T_{2G}$ was obtained to be $\approx 3830 \text{ s}^{-1}$. This value is close to the observed value of $2600\text{--}3000 \text{ s}^{-1}$.

Thus, the T_{2G} decay process entirely originates from the second moment of the direct homogeneous nuclear dipole-dipole interaction. On the other hand, the development of the Lorentzian component T_{2L} below 0.5 K suggests narrowing of the homogeneous linewidth. This behavior can explain the loss of the signal intensity of the NQR spectra at low temperatures.

After the correction of the spin-echo decay rate $1/T_2$, $I \times T$ for each line is independent of temperature down to 0.075 K. This finding indicates that $1/T_2$ becomes progressively larger with decreasing temperature and excludes the possibility of a wipeout phenomenon due to a dynamical effect caused by some distribution of the characteristic frequency of the spin fluctuation.

As discussed above, there is no anomaly in $1/T_1$ down to 0.075 K, on the other hand, the $1/T_2$ becomes larger below 1 K. In the last part of this section, we try to discuss the relationships between these behaviors and multipole fluctuations. As shown in Eq. (5.41), magnetic octupoles T_{xyz} can couple with a Nb nuclear spin at $[1/2, 1/2, 1/2]$ like $(I_x + I_y + I_z)\tilde{C}_{\text{Nb}}T_{xyz}$ form. Since there is threefold rotation axis around the $[111]$ directions, the octupole hyperfine coupling tensor must be isotropic. In such a case, fluctuating octupoles create fluctuating internal field parallel to $[111]$ direction, which corresponds to the quantization axis of the Nb nuclear spin in the NQR case. Then, in principle, this fluctuating field can contribute to the T_2 process but cannot contribute to the T_1 process because only the transverse component of the fluctuating field can contribute to the longitudinal relaxation as discussed in §3.

Therefore, the long range orders of dipoles and higher order multipoles are unlikely down to 0.075 K at zero field in $\text{PrNb}_2\text{Al}_{20}$. However, the decrease of $\Delta(1/T_{1f})/T$ and the enhancement of $1/T_2$ that occur below 1 K suggest the development of the short range correlation between the magnetic octupoles. The development of the correlation of the magnetic octupoles is also observed in the NMR measurement in PrAg_2In [63]. However, as discussed in the previous section, the hybridization is suggested to be weak in PrAg_2In . This implies that the fluctuations of 4f electrons arise from the direct f - f exchange interaction in PrAg_2In . In $\text{PrT}_2\text{Al}_{20}$, on the other hand, such a direct interaction between 4f electrons is weak because of the larger distance between Pr ions. Then, as indicated in the NMR measurements, c - f hybridizations are responsible for the 4f electronic fluctuations including multipole fluctuations at low temperatures.

6 Conclusion and outlook

The NMR/NQR studies are performed on the $\text{PrT}_2\text{Al}_{20}$ systems ($T = \text{Nb, Ta}$). From the field dependence of the Knight shift and the temperature independent $1/T_1$ at high temperatures, it is revealed that the localized nature of $4f$ electrons is important to understand the electronic states in $\text{PrT}_2\text{Al}_{20}$. However, the systematic comparison of the spin fluctuation rate Γ in $\text{PrT}_2\text{Al}_{20}$ compounds show that these systems have relatively strong c - f hybridizations in the Pr-based compounds.

In the measurement of $\text{PrTa}_2\text{Al}_{20}$, $1/T_1T$ suddenly decreases at around 1 K up to 19 T which corresponds to the bulk transition temperature. This result indicates that the ordering still survives at such a high magnetic field which may be related with the strong hybridization in $\text{PrTa}_2\text{Al}_{20}$.

In $\text{PrNb}_2\text{Al}_{20}$, however, such a clear anomaly is not observed in $1/T_1T$. Rather, the development of $1/T_1T$ with the broad maximum at around 0.7 K is observed up to 19 T. The field insensitive behavior of $1/T_1T$ corresponds to the bulk NFL behaviors at low temperatures, indicating the strong c - f hybridizations are important. From the NQR measurements, the absence of the long range magnetic dipole order down to 0.1 K with the enhanced ^{141}Pr nuclear magnetism clearly indicates the realization of the nonmagnetic ground state in $\text{PrNb}_2\text{Al}_{20}$ and the development of $1/T_2$ suggests the importance of the fluctuations of magnetic octupoles. Because the magnetic octupole fluctuations come from the interactions between electric quadrupoles and conduction electrons, the anomalous magnetic fluctuations observed in $\text{PrNb}_2\text{Al}_{20}$ have close relationships with the strong c - f hybridizations. In the future study, the measurement of the anisotropy of the magnetic fluctuations by using the single crystal NMR and the NQR measurements at Al sites can clarify whether the fluctuations captured by the NMR/NQR in the present study is truly of the magnetic octupole origin.

As an outlook, let us summarize the results from the viewpoint of the CEF states and hybridizations. It is suggested that $\text{PrTi}_2\text{Al}_{20}$ having Γ_3 - Γ_4 scheme has weaker hybridizations than other $\text{PrT}_2\text{Al}_{20}$ compounds having Γ_3 - Γ_5 scheme. This resembles that the relationship between the hybridizations and the CEF first excited state in Pr-based filled skutterudite. In addition, the estimated T_K is comparable to the CEF gap size between ground state and first excited state, then the quasi-quintet state consisted of the CEF doublet and triplet may dominate the low temperature properties. Such multiple degrees of freedom may be the origin of various low temperature phenomena in $\text{PrT}_2\text{Al}_{20}$ compounds.

In order to obtain a new aspect for c - f hybridizations in $\text{PrT}_2\text{X}_{20}$ systems, NMR/NQR studies for $X = \text{Zn}$ systems would be interesting. From the previous bulk and microscopic

studies, it is suggested that $X = \text{Zn}$ systems have weaker hybridizations than $X = \text{Al}$ systems. Then, the low temperature physics is expected to be dominated by pure Γ_3 doublet state. The estimation of T_K by using NMR/NQR would help us to compare the hybridization systematically in $\text{PrT}_2\text{X}_{20}$ systems.

It is important to clarify the physics arising from the multiple degrees of freedom including the excited states for the understanding of the relationships between strong hybridizations and multipoles. In such a purpose, the evaluation of hybridizations by NMR is expected to play an important role.

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Publication list

1. T. Kubo, H. Kotegawa, H. Tou, R. Higashinaka, A. Nakama, Y. Aoki, and H. Sato, “ ^{27}Al and ^{93}Nb NMR/NQR studies on the Pr-based heavy fermion system $\text{PrNb}_2\text{Al}_{20}$ ”, JPS Conference Proceedings **3**, 012031-pp.1–5 (2014).
2. T. Kubo, Y. Kizaki, H. Kotegawa, H. Tou, Y. Nagano, N. Araoka, A. Mitsuda, and H. Wada, “Structural phase transition and superconductivity in LaPt_2Si_2 : ^{139}La - and ^{195}Pt -NMR studies”, JPS Conference Proceedings **3**, 017031-pp.1–6 (2014).
3. T. Kubo, H. Kotegawa, H. Tou, R. Higashinaka, A. Nakama, Y. Aoki, and H. Sato, “ ^{93}Nb - and ^{27}Al -NMR/NQR studies of the praseodymium based $\text{PrNb}_2\text{Al}_{20}$ ”, Journal of Physics: Conference Series **592**, 012093-pp.1–5 (2015).
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