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Title	Crystal Growth and Experimental Tests for New Magnetoelectric Effects in Metallic Antiferromagnets
Author(s)	齋藤, 開
Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第13126号
Issue Date	2018-03-22
DOI	https://doi.org/10.14943/doctoral.k13126
Doc URL	https://hdl.handle.net/2115/69412
Type	doctoral thesis
File Information	Hiraku_Saito.pdf



博士學位論文

Crystal Growth and Experimental Tests for New
Magnetoelectric Effects in Metallic Antiferro-
magnets

(金属反強磁性体における新しい電気磁気効果の実験的検証
及び結晶育成)

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学位取得：2018 年 3 月

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1 Introduction

The behavior of solids without space-inversion symmetry has been one of the most attractive topics in the modern condensed matter physics in the last 50 years, since they show interesting phenomena such as a variety of magnetoelectric (ME) effects and parity-mixed superconductivity. The intensive studies in the last decade have further revealed that an antisymmetric spin-orbit coupling, which becomes active by space-inversion symmetry breaking, plays a relevant role in these phenomena. [1-5]. Moreover, the very recent theoretical and experimental studies have revealed that the various magnetotransport properties can be better understood and categorized on the basis of spatially extended multipoles [6,7].

It is known that a Hamiltonian for anti-symmetric spin orbit coupling is written as,

$$\begin{aligned} H_{ASOC} &= \mathbf{g}(\mathbf{k}) \cdot \boldsymbol{\sigma} \\ &= (\mathbf{k} \times \nabla V(\mathbf{r})) \cdot \boldsymbol{\sigma} \end{aligned} \quad (1),$$

where $\mathbf{g}(\mathbf{k})$ denotes antisymmetric vector, $\boldsymbol{\sigma}$ a Pauli matrix, and $\nabla V(\mathbf{r})$ the gradient of potential. The origin of antisymmetric spin-orbit coupling is regarded as (i) intrasite spin-orbit coupling, (ii) hopping between the orbitals with different parities, and (iii) local parity mixing of the orbitals with different parities [8-10]. Since odd-parity crystalline electric field drives (iii), antisymmetric spin-orbit coupling becomes active in the system without space inversion symmetry. One of the most prominent feature in the recent theoretical advance is that this term exists on site and compensates each other, if the system has an inversion center while it does not have local inversion symmetry on ions. In addition, the recent theory revealed that such antisymmetric spin-orbit coupling can break global space inversion symmetry and affect the bulk properties of the system, when antiferroic order occurs in a degree of freedom of the ions on a non-centrosymmetric site.

As an example, let us consider a 1D zig-zag chain composed of a kind of ion [11]. The chain has the space inversion center at the midpoint of the nearest neighbors while the ion site is not centrosymmetric. The gradient of the crystalline electric field, $\nabla V(\mathbf{r})$, shows a staggered arrangement (Fig. 1-1). If an antiferroic order with $+ - + -$ arrangement of magnetic moments lying along the x axis occurs, a toroidal moment, which is a kind of multipoles and defined as $\mathbf{t} \propto \sum_l \mathbf{r}_l \times \mathbf{S}_l$, is aligned along the z axis. Thus, such the antiferromagnetic order can be regarded as ferroic toroidal order. In addition, such a ferroic multipole order produces various exotic off-diagonal responses such as the ME effects [5]. These theories might provide a possible paradigm shift of solid state physics; The order known as usual antiferroic ones can be regarded as multipole order and may has unusual magnetotransport properties.

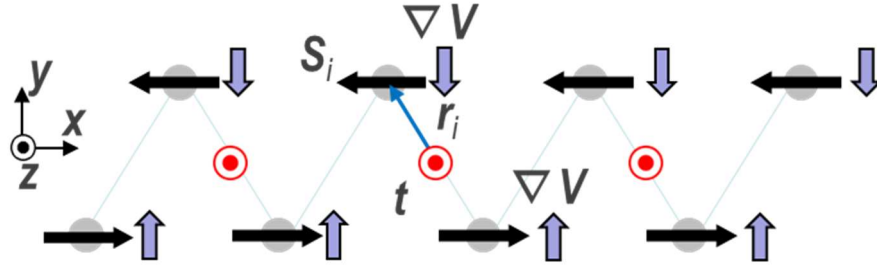


Fig. 1-1. A schematic image of toroidal moment on a 1D zig-zag chain formed by a kind of ions (gray circles). Bonds between the ions are guide to the eye. Black arrows are spin $\mathbf{S}_i$, purple arrows are the gradient of crystalline electric effect ∇V , red arrows are toroidal moment $\mathbf{t}$, blue arrow is position vector $\mathbf{r}_i$ from the inversion center, i denotes each ion site.

Though the presented theories have a great importance in the modern solid state physics, particularly related with the role of spin-orbit coupling, thus far only a few experimental studies have been made for the off-diagonal responses on the systems without local space inversion symmetry. A notable recent work would be the anomalous Hall effect found in Mn_3Sn , which can be explained on the basis of an off-diagonal ME response under a ferroic order of the extended magnetic octupole [12]. Thus, in the current situation of the research, it is highly desired that more experimental studies to be made to test a variety of attractive theoretical predictions.

1.1 The scope of the study

In this thesis, I focused on a theory describing exotic properties of toroidal moment and toroidal order on metallic systems given by S. Hayami *et al.* [13]. In order to test the prediction of their theory, we have performed magnetization measurements under electric currents on UNi_4B , which is a candidate metallic compound with a toroidic arrangement of magnetic moments. This work will be shown in Chapter 2. Then, the results of magnetization measurements on CeRh_2Si_2 will be presented in Chapter 3. CeRh_2Si_2 has two types of antiferromagnetic ordering with collinear magnetic moments of Ce ions, which are located at a centrosymmetric site. The study is aiming at obtaining a part of necessary conditions for the ME effects in metallic compounds. In Chapter 4, an improvement of single-crystal growth with a zone-melting method will be presented.

2 Magnetization measurement under electric current on UNi₄B

2.1 The aim of this work

In this Chapter, we first present a brief introduction of the recent theory on toroidal moment. Then, we present the experimental techniques, followed by the results of magnetization measurements under electric currents on UNi₄B.

Recently, Hayami *et al.* have predicted that the ferroic toroidal ordered metals may show various exotic phenomena such as band splitting, non-reciprocal optical response, current-induced magnetization, anomalous Hall effect under zero magnetic field, and so on [13]. They have also suggested that the magnetic structure in the antiferromagnetic ordered state of metallic UNi₄B can be regarded as the ferroic arrangement of toroidal moments. Then, we decided to perform magnetization measurements on UNi₄B under electric currents to test the reliability of the theoretical predictions. The reason why we chose the magnetization measurements to test the theory is simply because this measurement technique has little ambiguity yet high sensitivity for the extraction of the current-induced contribution.

2.2 Toroidal moment and ME effect

A toroidal moment is the lowest-rank term of toroidal multipole tensors which appear in the multipolar expansion of an electromagnetic vector potential [14]. It can be active in the system without local space-inversion symmetry on the relevant ion sites. It describes a composite of magnetic and electric degrees of freedom. In a spin ordered system, the toroidal moment $\mathbf{t}$ is defined as the summation of the vector products of position vector $\mathbf{r}_l$ and spin $\mathbf{S}_l$ for magnetic sites l :

$$\mathbf{t} = \frac{g\mu_B}{2} \sum_l \mathbf{r}_l \times \mathbf{S}_l \quad (2).$$

The summation is taken over appropriate magnetic basis. In a system where toroidal moments order with a ferroic component, both time-reversal and global space-inversion symmetries are broken, and thus macroscopic ME effects can be expected to occur. For example, ME properties seen in high magnetic fields in a traditional multiferroic system Cr_2O_3 [15] and a novel nonreciprocal directional dichroism observed recently in LiCoPO_4 [16] are described on the basis of the concept of toroidal order. The toroidal moment has so far been discussed mainly in insulating systems, where $\mathbf{r}_l$ corresponds to an electric dipole (electric polarization), and the presence of toroidal moment in a system can easily be recognized.

Recently, Hayami *et al.* have investigated possible toroidal ordering in a metallic system with broken local-inversion symmetry at magnetic-ion sites [13]. They predicted that exotic magnetotransport and ME effects can occur under the toroidal order, as a consequence of site-dependent antisymmetric spin-orbit coupling, off-site hybridization between orbitals with different parities, and an odd-parity crystalline electric field. Specifically, they performed a mean-field analysis for a single-band model on a layered honeycomb structure formed by one type of magnetic ion, and show that a ground state with the occurrence of spontaneous *toroidization* $\mathbf{T}$ (mean toroidal moment per unit volume) perpendicular to the layer planes is stabilized. The most notable consequence in their theoretical study will be the prediction of two types of ME response: one is net $\mathbf{T}$ induced by an electric current perpendicular to the planes, which occurs even in paramagnetic state, and the other is a uniform transverse magnetization induced by an electric current along the planes. Interestingly, they pointed out that an antiferromagnetic (AF) ordered state in UNi_4B corresponds to the ferroic toroidal order on a honeycomb structure, and thus may show the expected ME responses. In the present study, we have tested these theoretical predictions by measuring static magnetization of UNi_4B under applied electric currents. Note that the phenomenon of current-induced magnetization itself has quite recently been observed in a semiconductor, tellurium, even in the absence of any magnetic ordering [17].

2.3 The physical properties of UNi₄B

It is currently considered that UNi₄B crystallizes in the orthorhombic structure with the symmetry $Cmcm$ (No. 63, D_{2h}^{17}), where the U ions form a pseudo triangular-lattice layered structure in the a -plane of the orthorhombic structure. Lattice parameters a , b , and c are 6.968 Å, 17.1377 Å, and 14.8882 Å, respectively [18]. Once it had been reported to be the CeCo₄B-type hexagonal structure involving a perfect triangular lattice of U [19]. Thereafter, recent high resolution [18] and synchrotron X-ray [20] studies revealed slight deformation of the crystal structure from the hexagonal symmetry and different site occupation of Ni and B atoms. Since the observed magnitude of the lattice distortion is very small and undetectable by the laboratory X-ray Laue diffraction, we use hexagonal notation to describe the crystal directions of this system for simplicity in the present paper. The a -axis in orthorhombic notation, which is normal to the triangular lattice plane, corresponds to c in hexagonal one. We should, however, note that the U sites are actually not the space-inversion center, unlike in the hexagonal structure.

Neutron scattering studies show that UNi₄B exhibits an AF order at $T_N = 20.4$ K. In this ordered state, only 2/3 of U ions participate the ordering and the magnetic moments lies in c plane, forming a periodic array of vortex-like magnetic clusters in the shape of a hexagon as shown in Fig. 2-1(b) [21]. This magnetic cluster is equivalent to the definition of a toroidal moment. Thus, we describe the AF state of UNi₄B below T_N as ferroic order of spontaneous toroidal moments pointing to $[0001]$, if the reported magnetic structure is correct. The analyses of the neutron study, however, was made assuming the hexagonal structure, and thus may involve an ambiguity in the obtained magnetic structure, which we will discuss later. It is also reported that UNi₄B shows another phase transition at $T^* = 0.3$ K, where magnetic moments of the remaining 1/3 of U ions may order antiferromagnetically [22].

2.4 The experimental details

In the present work, the DC magnetization was measured using a commercial SQUID magnetometer (MPMS, Quantum Design Inc.) in the temperature range from 5 to 50 K under magnetic field up to 30 G. A single-crystalline sample was grown by the Czochralski pulling method using a tri-arc furnace, and confirmed to be a single phase from powder X-ray diffraction. No further heat treatment was performed. The crystal was cut into rectangular parallelepiped shape with typical dimensions of $\sim 1.8 \times 2.4 \times 0.2 \text{ mm}^3$ using a spark erosion machine.

In order to apply electric currents to the sample and check the electrical resistivity, four copper wires with a diameter of 0.026 mm were introduced from the top of a sample probe intended for the DC-mode magnetization measurements in MPMS. The four wires were attached to the edges of the longer side of the samples using conductive silver paste. The electric currents were applied using the DC current source, Model 6220 (Keithley Instruments Inc.).

The measurements were performed in the conditions of the electric currents I parallel to $[2\bar{1}\bar{1}0]$ and $[0001]$, which are expected to correspond to the directions perpendicular and parallel to T , respectively. Two voltage terminals were used for checking the electric currents flowing through the samples. All the measurements were performed in the conditions of cooling under magnetic field B (field cooling, FC) and a direct current (current cooling, CC) in order to reduce possible domain effect. Sample dimensions and measurement conditions are summarized in Table 1-1.

Tab. 1-1. Summary of measurement conditions. a , b , c means the crystal axes $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$, and $[0001]$, respectively. B and i are applied magnetic field and electric current density.

$a \times b \times c$ (mm ³)	orientation	B (G)	i (kA/m ²)
$2.4 \times 1.8 \times 0.2$	$i \parallel a, B \parallel b$	30	0, ± 27.8 , ± 41.7 , ± 55.6 , ± 69.4
		-5	0, ± 55.6
$0.2 \times 2.4 \times 3.1$	$i \parallel c, B \parallel b$	30	0, ± 20.8 , ± 41.7
		1	0, ± 41.7

2.5 How to analyze the data

Figure 2-1(a) shows an example of raw voltage signals V that are scaled by experimental factors as a function of position x , which are obtained by sweeping a sample through a second-derivative gradiometer (a set of pick-up coils) of the SQUID magnetometer, with applying B of 30 G and I of 20 mA to the sample. This value of I corresponds to the magnitude of electric current density, $i = 55.6 \text{ kA/m}^2$. In the standard magnetization measurements, the waveforms of $V(x)$ become symmetric, while those of the present measurements under electric current are obviously not. This is mainly due to the additional magnetic flux generated by I flowing through the sample and leads. We assume that this background signal is independent of temperature, and subtract the $V_0(x)$ data taken at 30 K in the paramagnetic state from other temperature data for each field-current condition. The results of such a subtraction procedure for the data profile in Fig. 2-1(a) are given in Fig. 2-1(b).

The obtained relative variations of the SQUID output voltage, $\Delta V(x) = V(x) - V_0(x)$, are still slightly asymmetric, showing a distortion from the standard formula in the position range below $\sim 2.5 \text{ cm}$. This indicates that there is some unknown weak background that depends on temperature and cannot be subtracted only by using the data at 30 K. Therefore, we use the $\Delta V(x)$ waveforms in the range $2.7 < x < 6.0 \text{ cm}$ for evaluating the magnetization in the present analyses. The solid curves in Fig. 2-1(b) indicate the results of the best fitting obtained by using the standard formula for the SQUID output voltage:

$$V(x) = \gamma m \left\{ 2 \left(\frac{1}{R_c^2 + (x + \delta)^2} \right)^{\frac{3}{2}} - \left(\frac{1}{R_c^2 + (x + \delta + L)^2} \right)^{\frac{3}{2}} - \left(\frac{1}{R_c^2 + (x + \delta - L)^2} \right)^{\frac{3}{2}} \right\} + \alpha + \beta x \quad (3),$$

where α denotes constant offset, β a linear drift, $\gamma (= 0.9125)$ a constant correction factor, $R_c (= 0.97 \text{ cm})$ the radius of pickup coils, $L (= 1.519 \text{ cm})$ the coil separation, m magnetization of the sample in emu, δ a shift of position

along x [23]. Magnetization M in μ_B/U ion is calculated from m and sample mass. All the data of M presented below were obtained in the same manner. Note that M obtained this procedure is the relative change from the 30 K data.

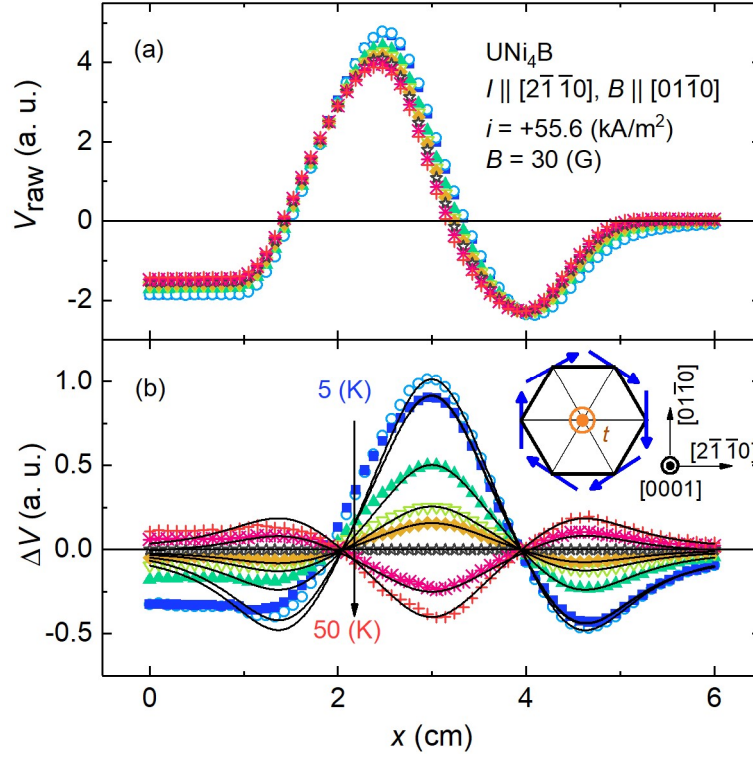


Fig. 2-1. (a) Raw SQUID voltage V_{raw} and (b) its relative variation ΔV_{raw} from the 30 K data versus position x . Solid curves indicate results of best fitting with Eq. (2) for the fitting range $2.7 < x < 6.0$ cm. The inset of panel (b) is a schematic drawing of toroidal moment $\mathbf{t}$ on UNi₄B in hexagonal notation viewed from [0001]. Blue arrows indicate magnetic moments.

2.6 Current-induced magnetization for $I \parallel [2\bar{1}\bar{1}0]$ and $B \parallel [01\bar{1}0]$

2.6.1 The experimental results

Figure 2-2(a) shows the temperature dependence of M measured at 30 G in the direction of $[01\bar{1}0]$ for $i = 0, \pm 27.8, \pm 41.7, \pm 55.6$, and ± 69.4 kA/m² applied along $[2\bar{1}\bar{1}0]$. We found that negative (positive) electric currents parallel to $[2\bar{1}\bar{1}0]$ cause positive (negative) changes of M in the direction of $[01\bar{1}0]$ below around T_N , respectively. By subtracting the data of 0 mA from those obtained under applied electric currents, the net component of magnetization, ΔM , induced by the currents is obtained as shown in Fig. 2-2(b). ΔM is almost constant (nearly zero) in the paramagnetic state for all the electric currents, while its magnitude of ΔM increases significantly as the temperature is lowered below T_N . All the ΔM curves are weakly winding in the temperature range 11 to 18 K. This behavior is considered to come from the error associated with the effects of Joule heating on the sample. As can be seen in Fig. 2-2(a), the magnetization in the $[01\bar{1}0]$ direction of the present system shows a strong increase with decreasing temperature in the above temperature range. Therefore, the magnetization data taken under electric currents are apparently shifted downward from their intrinsic values in this temperature range, if the temperature of the sample is higher than that of a thermometer. This inevitable temperature gradient due to applied electric current is considered to cause the shallow minimum of the ΔM curves in the subtraction procedures at around 13 K which is irrespective of the current direction. This speculation is also supported by the experimental fact that the "winding" behavior of ΔM becomes more significant with increasing the electric-current density (Fig. 2-2(b)), but remains insignificant at the lower magnetic fields, which will be presented later. A sharp break of ΔM at ~ 20 K for $i = +55.6$ kA/m² can also be ascribed to an apparent shift of T_N due to the weak heating-up of the sample.

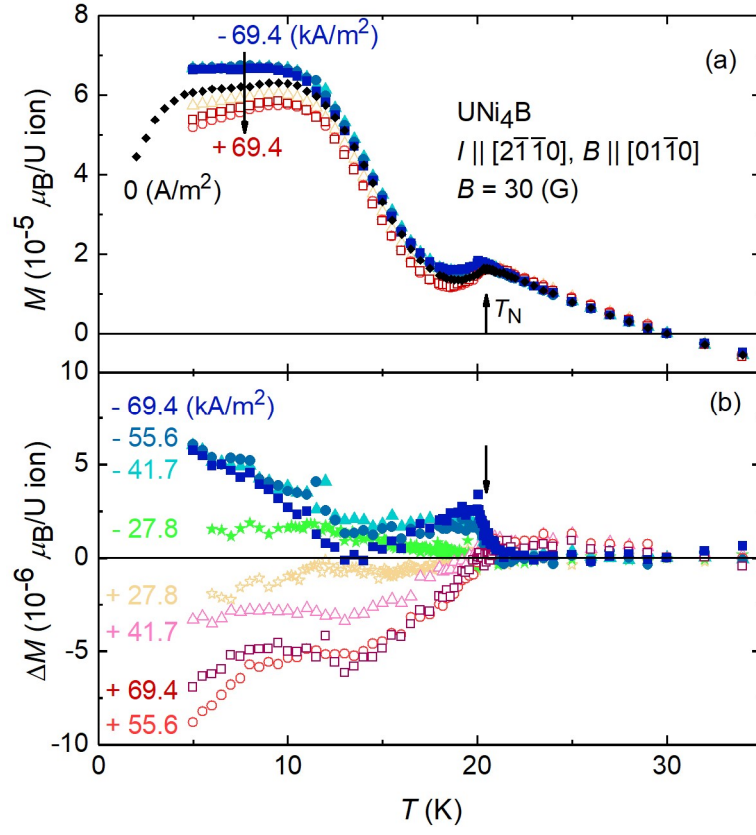


Fig. 2-2. (a) Magnetization M and (b) current-induced part of magnetization ΔM versus T for various magnitudes of electric current density $i \parallel [2\bar{1}10]$.

Figure 2-3 shows the values of ΔM for $i \parallel [2\bar{1}\bar{1}0]$ at 6 K and 30 G as a function of i . It is obvious that ΔM is in proportion to i in the range of the applied electric currents within the experimental accuracy. The rate of increase $d(\Delta M)/di$ is estimated to be $\sim 9.4 \times 10^{-11} \mu_B/U$ per unit current density. We would like to emphasize again that the sign of ΔM is altered by reversing the direction of I . Figure 2-4 shows M taken in the same B - I geometry for $i = 0$ and $\pm 55.6 \text{ kA/m}^2$ at a weaker magnetic field of -5 G, which is a remanent field of the MPMS superconducting magnet in this run. We observed that the obtained ΔM shows essentially the same behavior as that for $B = 30 \text{ G}$ (the inset of Fig. 2-4). The "winding" behavior due to the Joule heating is insignificant here because of a weaker temperature variation of M for $i = 0$. The $|\Delta M|$ value at $\sim 6 \text{ K}$ for $i = \pm 55.6 \text{ kA/m}^2$ is estimated to be $\sim 7 \times 10^{-6} \mu_B/U$, which is independent of the magnitude and the sign of magnetic field.

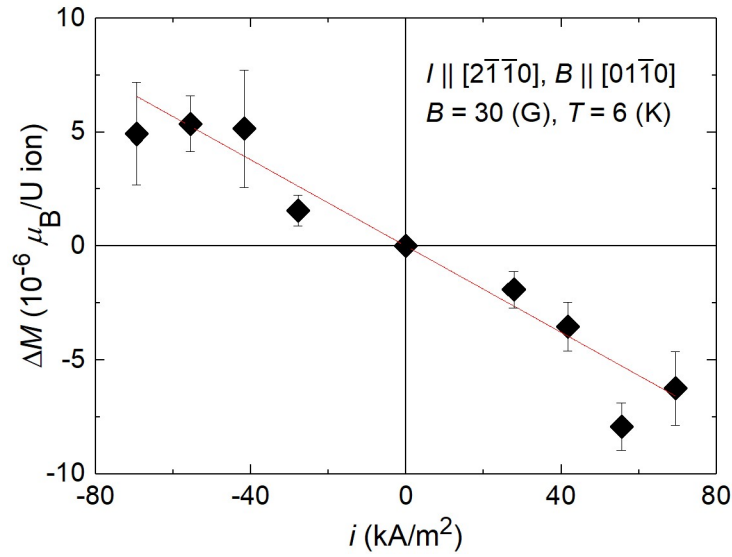


Fig. 2-3. ΔM versus $i \parallel [2\bar{1}\bar{1}0]$. The red line is the result of linear regression.

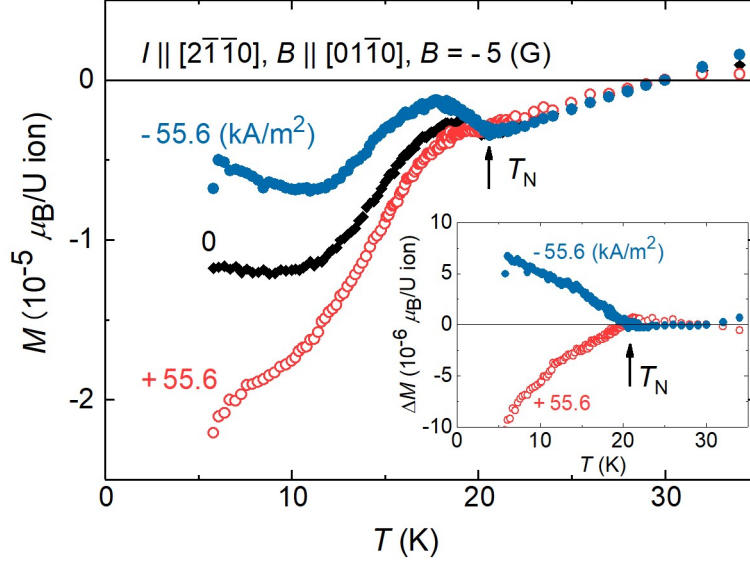


Fig. 2-4. M and ΔM (the inset) versus T for $i = \pm 55.6 \text{ kA/m}^2$ ($\parallel [2\bar{1}\bar{1}0]$) and $B = -5 \text{ G}$ ($\parallel [01\bar{1}0]$).

2.6.2 The extrinsic components as a possible cause of ΔM

One might think that the observed behavior of ΔM would be an extrinsic phenomenon, since the magnetic flux generated by the electric currents has a temperature dependence which cannot fully be eliminated by the subtraction of 30 K data. Since the present measurements were performed under the constant electric current, such an effect should be independent of a change in the electrical resistivity of the circuit, which is composed of the sample and the Cu wires. The only possible cause in the present circuit would be a change in the shape of the circuit due to thermal expansion. However, a relative change in the sample length below 50 K is negligibly small ($\sim 10^{-6} \text{ K}^{-1}$) [24], and thermal expansion of the Cu wires does not explain the fact that a sharp change in ΔM occurs at T_N .

We would also like to mention a possible surface effect. Since the Rashba-type antisymmetric spin-orbit coupling is always active on the surface of a metal, the observed ME phenomenon might be ascribed to a property of the surface states. To test this possibility, we repeated the measurements using the same sample piece after oxidizing the surface in the air; the oxide thickness was estimated to be ~ 0.03 nm by comparing the sample thickness before and after etching. Since the sequence of interfaces changes from metal-vacuum to metal-oxide-vacuum, the oxidization of the surface should affect the strength of the Rashba-type spin-orbit coupling, resulting in a change in the ME effects. However, we observed no significant difference in the behavior of ΔM between the measurements with oxidized and non-oxidized surfaces. We therefore naively suggest that the observed current-induced magnetization in UNi₄B is not simply attributed to the surface effect.

On the basis of these experimental results and consideration, we conclude that the change observed in ΔM parallel to $[01\bar{1}0]$ below T_N is intrinsic to the application of $\mathbf{i}$ along the $[2\bar{1}\bar{1}0]$ direction. This is consistent with the theoretical prediction that uniform magnetization can be induced in the direction of $\mathbf{T} \times \mathbf{i}$.

2.7 Current-induced magnetization for $I \parallel [0001]$ and $B \parallel [01\bar{1}0]$

2.7.1 The experimental results

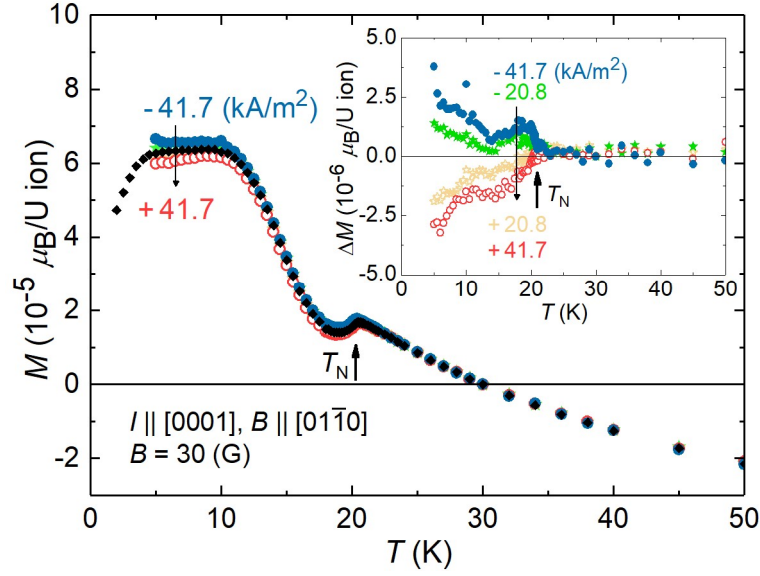


Fig. 2-5. M and ΔM (the inset) versus T for $i = \pm 20.8$ and ± 41.7 kA/m² ($\parallel [0001]$) and $B = 30$ G ($\parallel [01\bar{1}0]$).

Figure 2-5 shows the experimental results obtained in the different geometry: $M \parallel [01\bar{1}0]$ under $i \parallel [0001]$ at $B = 30$ G. Obviously, $M(T)$ is enhanced or suppressed below and near T_N by applying electric currents in positive or negative directions, respectively. The obtained ΔM stays nearly constant in the paramagnetic state, while changes as the temperature is lowered below T_N (the inset of Fig. 2-5), roughly in proportion to the magnitude of i . The winding feature with a shallow minimum at ~ 13 K of ΔM is considered to be due to the effects of Joule heating on the sample, as mentioned above.

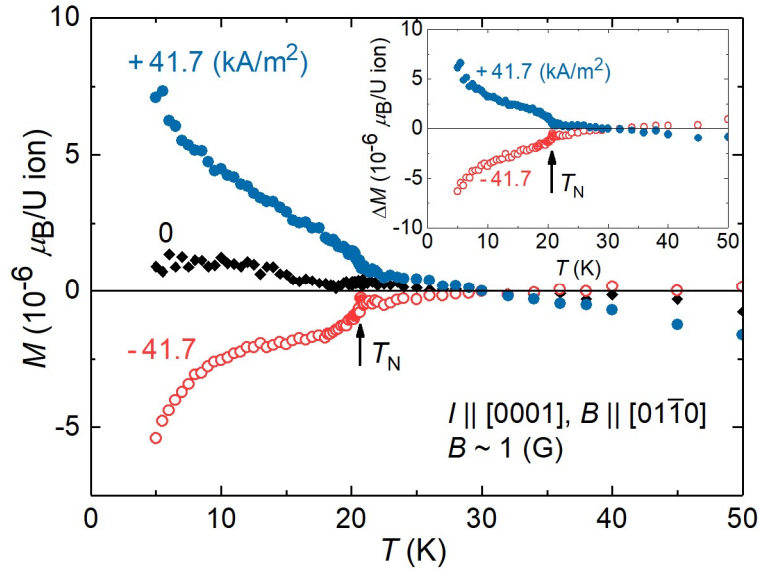


Fig. 2-6. M and ΔM (the inset) versus T for $i = \pm 41.7 \text{ kA/m}^2$ ($\parallel [0001]$) and $B \sim -1 \text{ G}$ ($\parallel [01\bar{1}0]$).

Figure 2-6 shows the experimental results obtained in the same current-field geometry at a weaker magnetic field of $\sim 1 \text{ G}$ (again, the remanent field in this run). The reduction of the applied magnetic field makes the temperature variation of ΔM clearer, obscuring the heating-up effects. The absolute magnitude of ΔM at 6 K and $\pm 41.7 \text{ kA/m}^2$ is estimated to be about $5 \times 10^{-6} \mu_B/U$, which is slightly smaller than that for $M \parallel [01\bar{1}0]$ and $i \parallel [2\bar{1}\bar{1}0]$.

According to the theory published by Hayami *et al.*[13], $\mathbf{i} \parallel [0001]$ of UNi_4B may induce the change of toroidalization, $\Delta\mathbf{T}$, in the same direction as $\mathbf{i}$. This may occur even in the paramagnetic state, where microscopically the vortex-like arrangement of magnetic moments, *i.e.*, the AF structure of this system, is induced. Below T_N , on the other hand, the ferroic order of the toroidal moment $\mathbf{t}$ occurs spontaneously, forming two domains with $\mathbf{T} \parallel [0001]$ or $[000\bar{1}]$. In each domain, the toroidalization can be enhanced ($\mathbf{T} + \Delta\mathbf{T}$) or suppressed ($\mathbf{T} - \Delta\mathbf{T}$) for $\mathbf{T}$ parallel to $+\mathbf{i}$ or $-\mathbf{i}$, respectively. Microscopically, this corresponds to an enhancement or a suppression of the ordered magnetic moments at U sites. In principle, such a change in magnetic moments can be detected by measuring magnetization with magnetic fields applied along the basal (0001) plane, if the two domains have different volumes. Moreover, in this case, ΔM should depend on B . In the present measurements for $\mathbf{i} \parallel [0001]$, however, its magnitude is almost independent of B . This behavior is significantly different from the theoretical prediction.

2.7.2 The possible causes of the inconsistency

One reason of the above inconsistency could be a path that electric currents flow through in a sample. In the measurements for $i \parallel [0001]$, we used a sample piece which has a rectangular parallelepiped shape with a width of ~ 2.4 mm and a thickness of $\times 0.2$ mm perpendicular to the current flow direction in a length of $\times 3.1$ mm. Therefore, the currents that flow through the sample may have a component in the basal (0001) plane, which could result in the ΔM as we observed for $i \parallel [2\bar{1}\bar{1}0]$. In order to check this possibility, it is necessary to repeat the measurements using a sample with different dimensions. Our preliminary repeated trials, however, show no significant change in the behavior of ΔM thus far. We should note that the current path also depends on the anisotropy of the electrical resistivity ρ in general. The ρ of UNi₄B for $i \parallel [2\bar{1}\bar{1}0]$ is several times larger than that for $i \parallel [0001]$ [19]. Therefore, from the viewpoint of anisotropy in ρ , the deviation of electric currents from the [0001] direction will be unfavorable.

Another, more likely reason is derived from the ambiguity of the crystal and magnetic structures of the present system. Mentink *et al.* proposed vortex-like magnetic structure below T_N on the basis of their neutron diffraction measurements [19]. However, the analysis they made is based on the hexagonal CeCo₄B-type crystal structure, and the best fitting obtained among a few hundred candidate magnetic structures still has a large reliability factor $R = 11.8\%$. In addition, if the crystal structure is orthorhombic, $Cmcm$, as pointed out in the recent studies [18,20], the arrangement of Ni and B atoms surrounding U atoms differs largely from that in the hexagonal structure: the former has four inequivalent crystallographic U sites in a U-Ni-B layer, while the latter has two U sites forming U-Ni and U-B layer. The four U sites in the orthorhombic structure do not have the inversion symmetry, and thus may produce local toroidal moments which are different both in direction and magnitude at each U site. The inconsistency between the theory and the present experimental results might imply that these structures differ from the crystal and magnetic structures discussed so far.

2.8 Conclusion

In summary, we performed magnetization measurements under electric currents in the AF uranium compound UNi₄B. We have revealed that the application of electric currents parallel to $[2\bar{1}\bar{1}0]$ and $[0001]$ both induces static magnetization in the direction of $[01\bar{1}0]$ below T_N . The magnitude of ΔM at low temperature is estimated to be of the order of $10^{-10} \mu_B / U$ per unit current density. The observation is consistent with the recent theoretical predictions, in the sense that the ME effects may actually occur in a metallic system with broken local-inversion symmetry. However, there is a crucial inconsistency that ΔM is induced by the current flow $i \parallel [0001]$, which is an inactive geometry ($i \parallel T$) regarding the ME effects. In order to gain a better understanding of the origin of the observed phenomena, we need to complete the identification of crystal and magnetic structures of this system.

3 Magnetization measurement under electric current on CeRh_2Si_2

3.1 The aim of this work

As shown in Chapter. 2, the behavior of current-induced magnetization of UNi_4B has an inconsistency between the theoretical prediction and the experimental results, while it is surely observed below T_N . An ambiguity on magnetic and crystal structures of UNi_4B is considered to be one of a possible causes of this inconsistency. Since toroidal moment on this system can be estimated from the arrangement of magnetic moments and an odd-parity crystalline electric field at magnetic ion sites, the ambiguity of the fundamental magnetic and crystal structures leads to an ambiguity of the direction, arrangement and size of toroidal moment. This situation hinders us in the comparison between the theory and experiment.

In order to solve the above problem, we have been proceeding with two projects. One is searching other systems which show current-induced magnetization. The other is rechecking crystal and magnetic structure of UNi_4B . In this chapter, the former will be focused on. The goal of this work is to find the systems which show current-induced magnetization and reveal the requirements for the magnetoelectric effects in metallic systems from the experimental point of view. In this Section, we present the experimental results of magnetization measurement under electric current on CeRh_2Si_2 , which is a metallic system with two collinear antiferromagnetic orders, and reveal that this system shows clear ME effects in an ordered state.

3.2 Why is CeRh_2Si_2 chosen?

Since we do not have an appropriate database, we searched a proper material by surveying references one by one. Here, we present our strategy and policy on searching a new material to investigate magnetization under electric current.

a) Metallic system

This is a necessary condition to perform the experimental test for the predicted theory.

b) Collinear antiferromagnetic order

Antiferroic arrangement of magnetic moments will be the simplest requirement for a toroidal moment. In addition, from the experimental point of view, simpler crystal and magnetic structures would have an advantage on its reliability.

c) High symmetric crystal structure and magnetic ions on high-symmetry site

This is also for the purpose of simplicity. It is expected from the theory that magnetic ions on centrosymmetric site never have the ME effects. However, we have not achieved any experimental confirmation so far. Thus, a system with magnetic ions on centrosymmetric site are acceptable to confirm the absence of ME effects. In addition, from the experimental point of view, high symmetry of crystal has an advantage on the reliability of magnetic and crystal structures. For instance, in X-ray and neutron diffraction measurements, a high symmetric structure presents less Bragg peaks thanks to an extinction rule, resulting in the accurate analyses on crystal and magnetic structures.

d) T_N around 20 to 30 K

This condition is set to enable us to perform the measurements under mostly the same conditions as those for the study on UNi_4B . The experimental results will serve as useful reference of UNi_4B . T_N below 20 K is not preferable, because the low-temperature limit of the present experimental setup is not low (6K).

e) Including 4d/5d-electron elements

Since the spin-orbit coupling is a key of the predicted ME effects in the theory, the system is desired to include 4d and/or 5d elements with strong spin-orbit coupling.

f) U compound

To compare with UNi_4B , it is better to study U compound. We, however, could not find a good candidate, and thus used a Ce compound.

g) Hexagonal structure

This is also for the comparison with UNi_4B , but we could not find a good candidate with high T_N .

Finally, I chose CeRh_2Si_2 for the present study. The physical properties of this system will be presented in the next chapter. The deciding factor for the choice is that this system has two antiferromagnetic orders: one is magnetoelectrically inactive, while the other could be active.

3.3 The physical properties of CeRh_2Si_2

CeRh_2Si_2 crystallizes in the ThCr_2Si_2 -type tetragonal structure with the symmetry $I4/mmm$ (No. 139, D_{4h}^{17}) (Fig. 3-1). Lattice parameters are $a = 4.08 \text{ \AA}$ and $c = 10.15 \text{ \AA}$ (this work). Ce ions occupy a centrosymmetric site with the symmetry $4/mmm$.

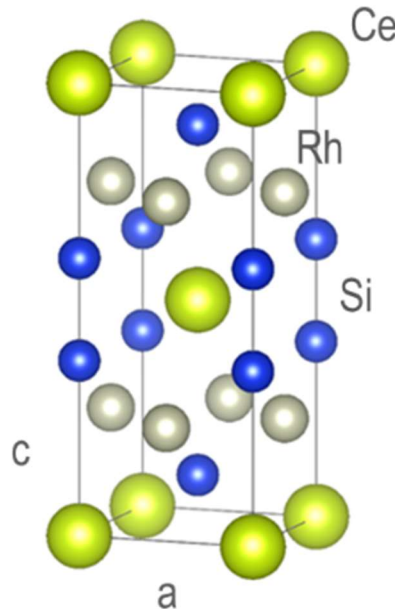


Fig. 3-1. Crystal structure of CeRh_2Si_2

CeRh_2Si_2 has two successive antiferromagnetic orders at $T_{\text{N1}} = 35$ K and $T_{\text{N2}} = 24$ K [25]. Several works of neutron-diffraction, NMR and μSR measurements revealed that Ce ions participate the ordering and these antiferromagnetic ordered phases are characterized by propagation vector $\mathbf{q} = (0.5, 0.5, 0)$ and $(0.5, 0.5, 0) + (0.5, 0.5, 0.5)$, respectively. In both cases, magnetic moments lie along $[001]$. Magnetic order below T_{N2} has two possible structures; one is the structure composed of two domains with $\mathbf{q} = (0.5, 0.5, 0)$ and $(0.5, 0.5, 0.5)$, and the other is a so-called 4- $\mathbf{q}$ structure which is homogeneous $\mathbf{q} = (0.5, 0.5, 0)$ structure with superimposed $\mathbf{q} = (0.5, 0.5, 0.5)$. The reported magnitude of ordered moment below T_{N2} has an inconsistency between neutron measurement ($\sim 1.5 \mu_{\text{B}}/\text{Ce}$) [26] and NMR measurement ($\sim 0.3 \mu_{\text{B}}/\text{Ce}$) [27]. The point is that some of space-inversion centers that CeRh_2Si_2 has are preserved in the above AF ordered phases. Thus, the symmetry considerations tell us that CeRh_2Si_2 cannot show the bulk ME effects below both of T_{N1} and T_{N2} . Note that a propagation vector $\mathbf{q} = (0.5, 0.5, 0.5)$ breaks space-inversion symmetry at Ce ion site. Then Ce ion can drive ME effect locally. However, it will be cancelled out because antiferroic local ME effect is expected to occur due to space-inversion symmetry in the unit cell.

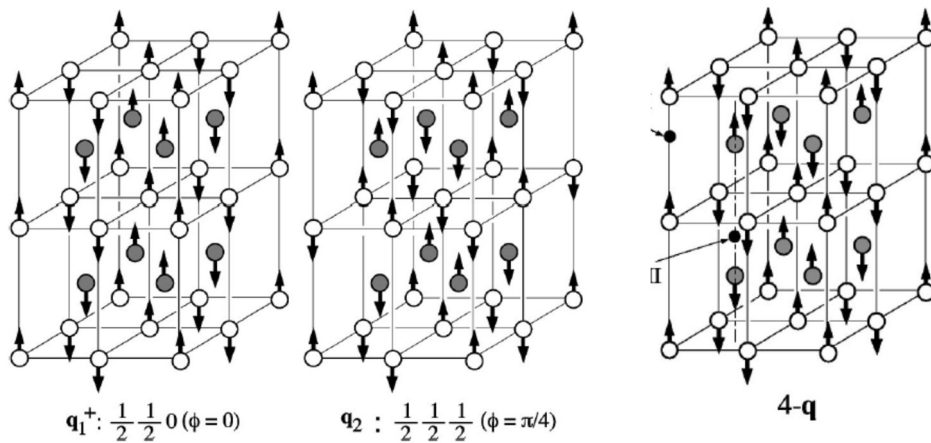


Fig. 3-2. Magnetic structures of CeRh_2Si_2 [28]

3.4 The experimental details

In the present work, the DC magnetization measurements were performed using a commercial SQUID magnetometer in the same manner as in the measurements on UNi₄B. The temperature range is 6 to 50 K under magnetic field applied up to 300 G. A single-crystalline sample was grown by the Czochralski method using a tetra-arc furnace. Starting materials are 3N (99.9% pure)-Ce, 4N-Rh, and 5N-Si. A single-phase composition was confirmed by using X-ray powder diffraction. The small mosaicity can be seen by Laue diffraction on the single-crystalline sample. No further heat treatment was performed. The crystal was cut into rectangular parallelepiped shape with typical dimensions $\sim 0.25 \times 1.25 \times 3.55 \text{ mm}^3$.

Only two Cu wires with a diameter of 0.026 mm were introduced into the sample probe of MPMS for this measurement. The wires are attached to the edges of the longer side of the samples. Since it is difficult in this case to realize a short circuit after making contacts with the sample, a short circuit was carefully checked during the sample setting. Magnetizations along [100] and [001] were measured in the conditions of the electric currents $\mathbf{I}$ parallel to [100] and [001]. Measurement conditions are summarized in Table 3-1.

Table 3-1. Summary of measurement conditions. a and c mean the crystal axes [100] and [0001], respectively. $\mathbf{B}$ and $\mathbf{i}$ are applied magnetic field and electric current density.

$a \times a \times c \text{ (mm}^3\text{)}$	Orientation	$B \text{ (G)}$	$i \text{ (kA/m}^2\text{)}$
$1.55 \times 3.25 \times 0.25$	$\mathbf{i} \parallel a, \mathbf{B} \parallel c$	30	0, ± 32 , ± 64
		-30	0, ± 32 , ± 64 , ± 96
		100	0, ± 64
	$\mathbf{i} \parallel \mathbf{B} \parallel a$	300	0, ± 32 , ± 64
$0.50 \times 0.78 \times 2.50$	$\mathbf{i} \parallel \mathbf{B} \parallel c$	30	0, ± 51.2
	$\mathbf{i} \parallel c, \mathbf{B} \parallel a$	100	0, ± 51.2

3.5 Current-induced magnetization for various settings

3.5.1 For $I \parallel [100]$, and $B \parallel [001]$

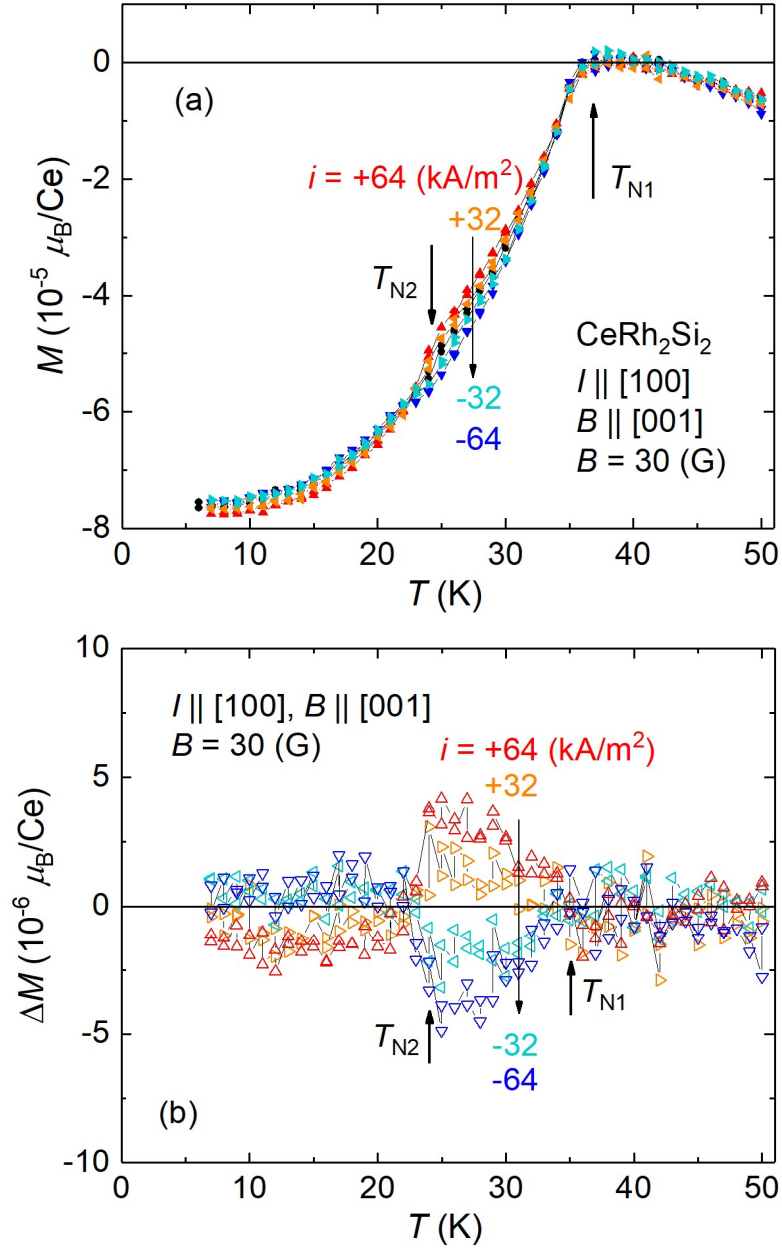


Fig. 3-3. (a) M and (b) ΔM ($\parallel [001]$) versus temperature for $i = \pm 32$, and ± 64 kA/m^2 ($\parallel [100]$) and $B = 30$ G.

Figure 3-1(a) shows the temperature dependence of magnetization measured at 30 G in the direction of [100] for $i = 0, \pm 32$, and ± 64 kA/m² applied along [001]. The data at each temperature are relative change from the data at 40 K, which we used for subtracting the extrinsic background signals. Surprisingly, we found that positive (negative) electric currents parallel to [100] cause positive (negative) changes of magnetization in the temperature range between T_{N1} and T_{N2} , where the system is expected to be in a magnetoelectrically inactive phase. These data are converted into the temperature dependence of current-induced part of magnetization ΔM as shown in Fig 3-1(b). ΔM is nearly zero in paramagnetic phase for all the electric-current values, while it increases significantly as temperature is lowered below T_{N1} , and then suddenly decreases to nearly zero at T_{N2} . The sign of ΔM between T_{N1} and T_{N2} is altered by reversing electric currents. ΔM below T_{N2} has small deviation from zero. We think that this is due to the existence of an extrinsic component which is changed gradually by cooling the system. Magnetic flux generated by applied electric currents distort the waveform of SQUID output voltage. This influence cannot completely be excluded by the subtraction of the data obtained at 40 K. Such distortion of the voltage signals also makes it difficult to exclude linear and constant background of the voltmeter by fitting using the standard formula (see also Chap. 2-4). Thus, ΔM might have these extrinsic components. This speculation agrees with the experimental data of ΔM below T_{N2} , where ΔM shows a current dependence and decreases by improving the setting (shown later in Fig. 3-6).

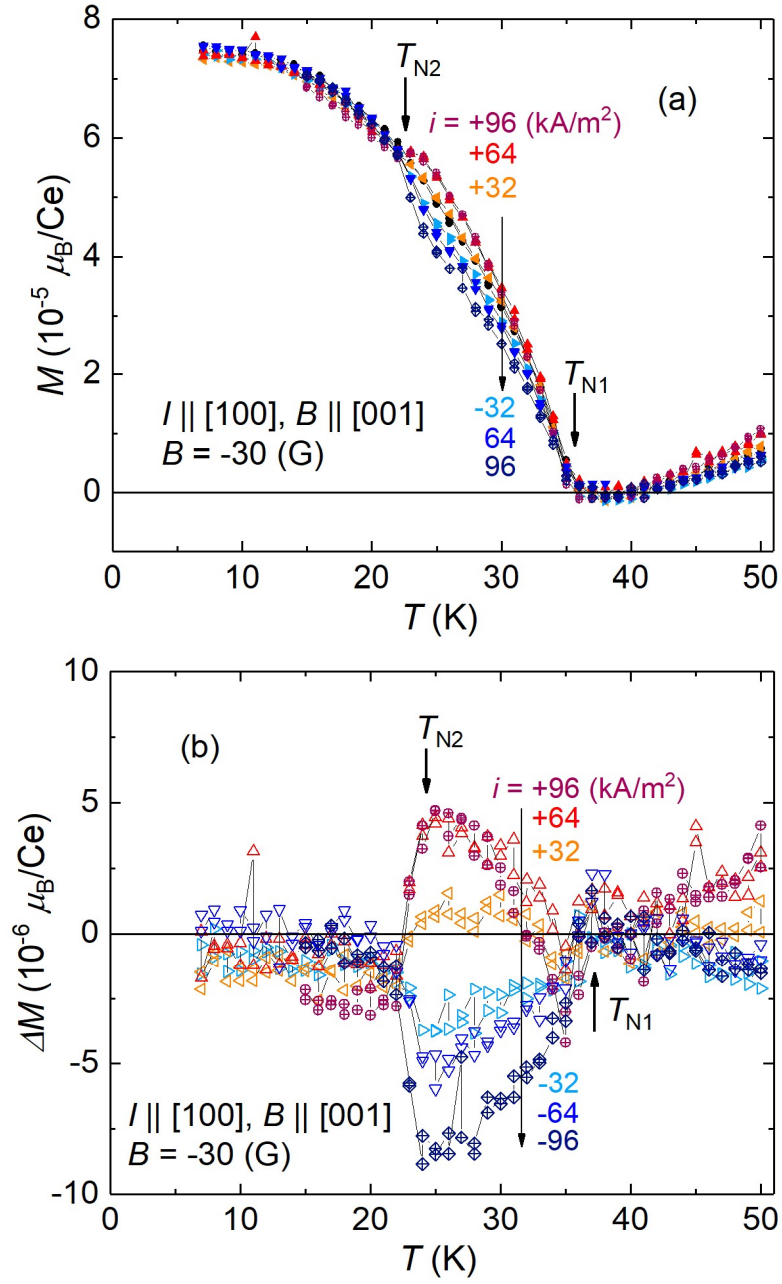


Fig. 3-4. (a) M and (b) ΔM ($\parallel [001]$) versus temperature for $i = \pm 32, \pm 64, \pm 96$ kA/m² ($\parallel [100]$) and $B = -30$ G.

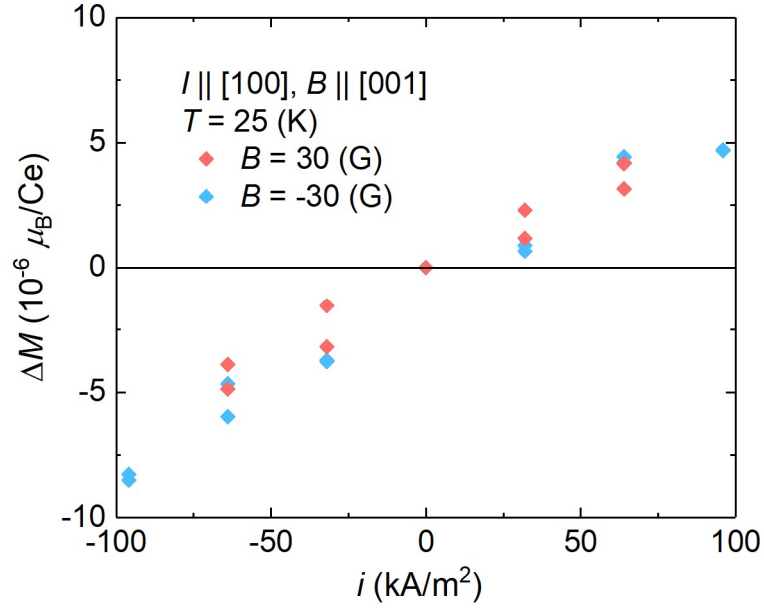


Fig. 3-5. ΔM ($\parallel$ [001]) versus i ($\parallel$ [100]) for magnetic field $B = \pm 30$ G and $T = 25$ K.

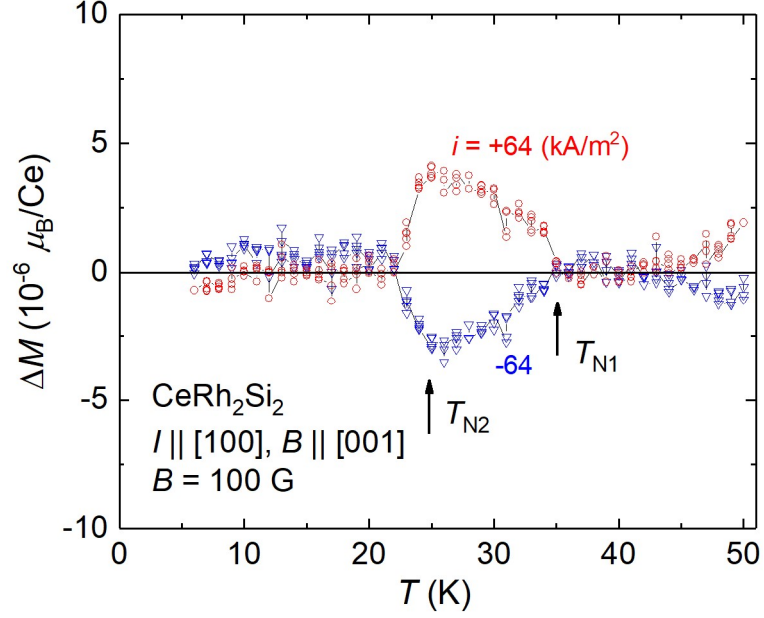


Fig. 3-6. ΔM ($\parallel$ [001]) versus T for $i = \pm 64$ kA/m² ($\parallel$ [100]) and magnetic field $B = 100$ G.

Figure 3-4 shows the data taken in the same B - I geometry for $i = 0, \pm 32, \pm 64$ and ± 96 kA/m², respectively at a reversed magnetic field of -30 G. Though the background component is larger than that at 30 G, ΔM below T_{N1} is still significant. The sign of ΔM is independent of the field direction. Figure 3-5 shows the values of ΔM for $i \parallel [100]$ at 25 K and ± 30 G as a function of i . Obviously, ΔM is in proportion to i within the accuracy of the measurement. Figure 3-6 shows the data taken in the same B - I geometry for $i = 0$ and ± 64 kA/m², respectively, at a higher field of 100 G. The sample is set again before this measurement and the measurement conditions are improved. ΔM below T_{N2} becomes almost zero. These observed features of ΔM is the same as those of UNi₄B. Thus, we can conclude that magnetization in the direction of $[100]$ is induced by electric currents applied along $[001]$ on CeRh₂Si₂ only between T_{N1} and T_{N2} . The possibilities of this phenomena will be discussed later.

3.5.2 For other settings

The same measurement was performed for other three settings. Figure 3-7 and 3-8 shows temperature dependence of ΔM for various electric currents. The geometries are (3-7) $\mathbf{I} \parallel \mathbf{B} \parallel [100]$, (3-8(a)) $\mathbf{I} \parallel \mathbf{B} \parallel [001]$, and (3-8(b)) $\mathbf{I} \parallel [001]$ and $\mathbf{B} \parallel [100]$. Since $M \parallel [100]$ is the magnetic hard axis of CeRh_2Si_2 , a relatively stronger magnetic field is applied to obtain better S/N. The inset is the temperature dependence of M for each setting. Note that the vertical axis is magnified twice the above ΔM - T viewgraph. As can be seen, the temperature dependence of ΔM for all of the three settings has no significant change at T_{N1} and T_{N2} , showing only a gradual deviation with the magnitude of currents and temperature.

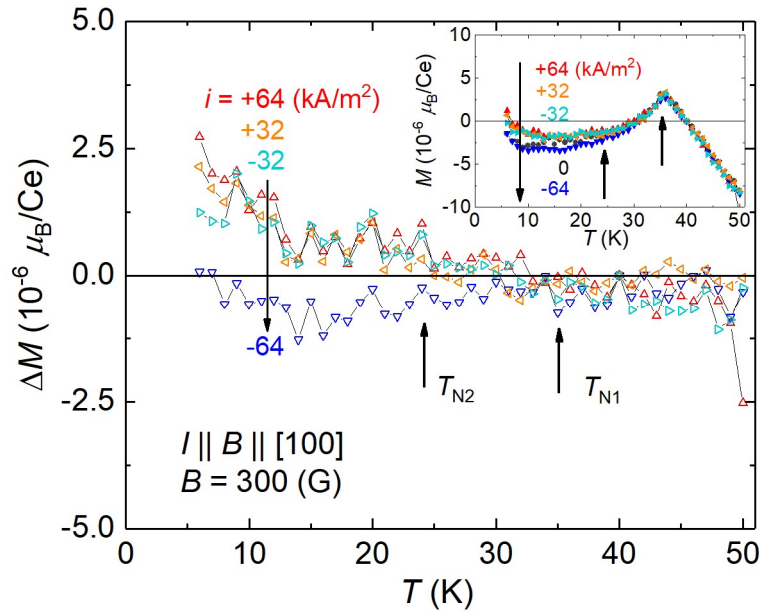


Fig. 3-7. ΔM ($\parallel [100]$) versus T for $i = \pm 32$ and ± 64 kA/m² ($\parallel [100]$) and magnetic field $B = 300$ G. (The inset) M versus T .

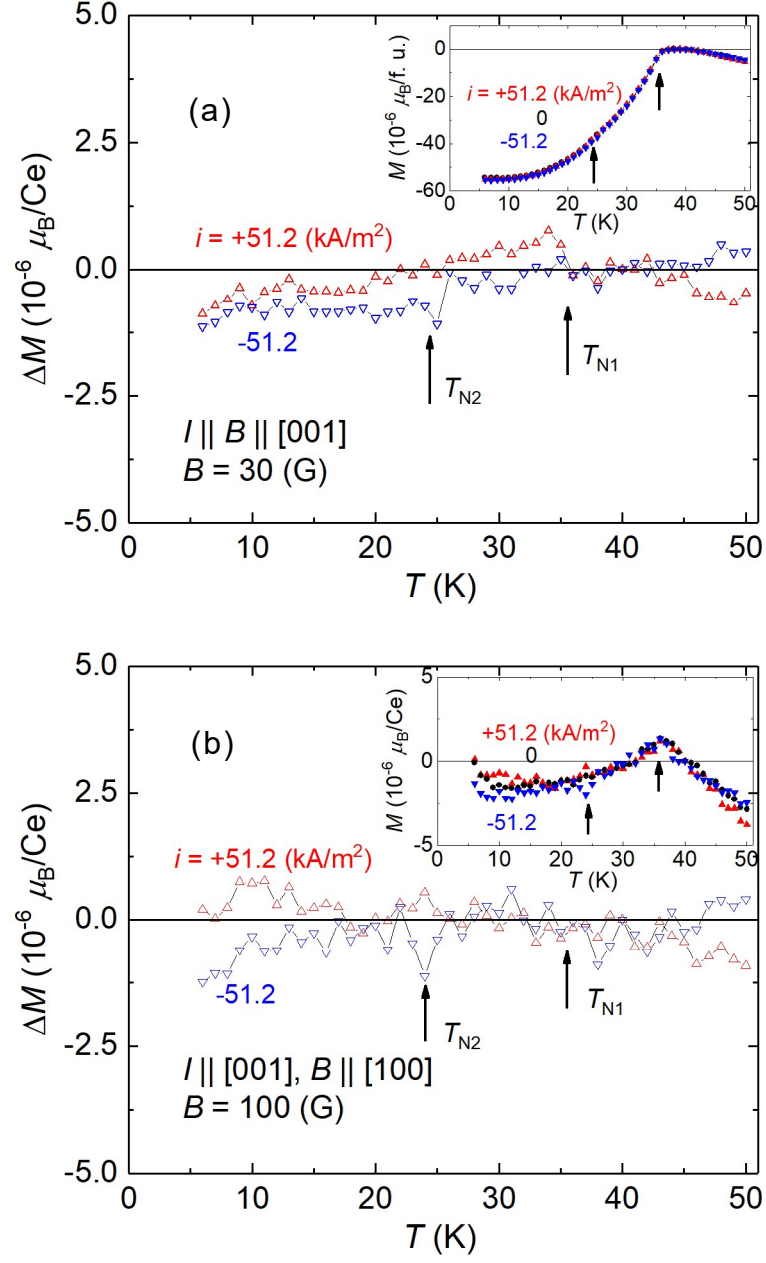


Fig. 3-8. ΔM versus T for $i = \pm 51.2$ kA/m² ($\parallel [001]$) and magnetic field $B =$ (a) 30 G ($\parallel [001]$) and (b) 100 G ($\parallel [100]$). (The insets) M versus T .

3.6 Possible cause of magnetoelectric effect on CeRh₂Si₂

Let us now consider the cause of the ME effects in CeRh₂Si₂. As mentioned above, CeRh₂Si₂ should not have any bulk ME effects in the present understandings. A peak in the ²⁹Si-NMR spectra, which indicates internal magnetic fields on the Si-ion site, splits into two peaks at T_{N1} (Fig. 3-9) [27]. This is consistent with the magnetic structure with the propagation vector $\mathbf{q} = (0.5, 0.5, 0)$. If space-inversion symmetry at Ce-ion site were broken, a peak in NMR spectra would split into more than two. However, it is reported in the previous papers that additional splitting was not observed in the accuracy of the measurement. Setting apart from previous reports, it might be useful to measure it again.

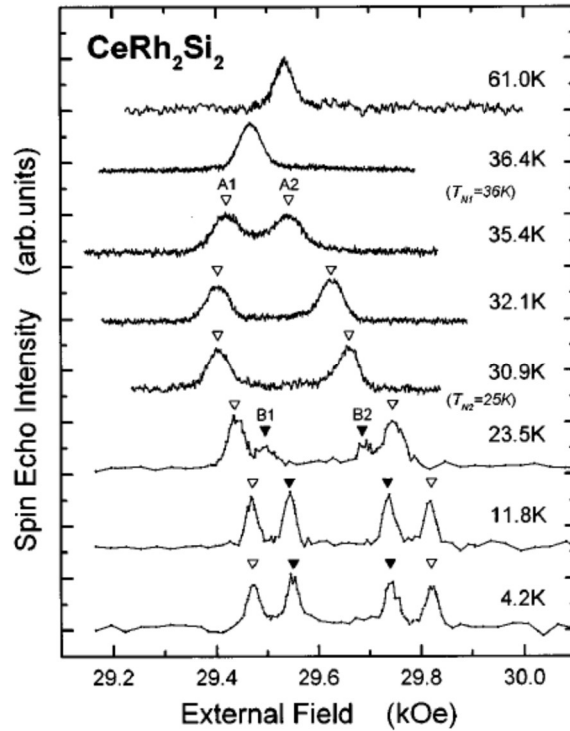


Fig. 3-9. ²⁹Si-NMR spectra of CeRh₂Si₂. The external field is applied along *c*. [27]

Then, what can be a cause? Hereafter, I would like to list up the possibilities and check them one by one.

- a) Surface effect
- b) Magnetic moment on Rh ions
- c) Macroscopic lattice distortion such as mosaicity
- d) Domain wall of magnetic structure

- a) Surface effect

Since the surface does not have space-inversion symmetry, Rashba-type antisymmetric spin-orbit coupling becomes active at the surface, resulting in the surface can be active magnetoelectrically. Let us calculate the magnetic moment, assuming that one layer on each of flat six surfaces of the rectangular parallelepiped sample participates in the ME effect. The number of Ce ions on the surface is about 3.4×10^{13} which can be calculated from the sample dimensions of $a \times a \times c = 0.25 \times 3.55 \times 1.25 \text{ mm}^3$ and lattice parameters of $a = 4.08 \text{ \AA}$ and $c = 10.15 \text{ \AA}$. It is 0.557×10^{-10} in the mol unit. On the other hand, molecule number in the bulk calculated from mass is $1.875 \times 10^{-5} \text{ mol}$. Thus, Ce ions on the surface should have the 10^5 times larger magnitude of magnetic moments than that for the bulk sample, for a quantitative explanation of the presently observed ME effects. That is roughly $1.2 \mu_B/\text{Ce}$ at $i = 64 \text{ kA/m}^2$ and $T = 25 \text{ K}$. This is too large, if taking into account of the saturated moment of $1.5 \mu_B/\text{Ce}$ at $B = 26 \text{ T}$. Therefore, it is difficult to ascribe the observed ME effects of CeRh_2Si_2 to the surface effect.

b) Magnetic moments on Rh ions

Rh ion is surrounded by tetrahedron of Si ions, so that Rh-ion site does not have space inversion symmetry. Therefore, if Rh ion participates in antiferromagnetic order at T_{N1} , it may cause the ME effects. However, all the previous NMR, neutron, and μ SR measurements, which were performed to investigate the magnetic structures of CeRh_2Si_2 have not reported any indication of the existence of a magnetic component on the Rh ion site [25-29]. Furthermore, very recent synchrotron X-ray measurement cannot find any magnetic peak intensities in the resonant X-ray (magnetic) scattering of the Rh ion [30].

c) Macroscopic lattice distortion such as mosaicity

Though a lattice distortion from the tetragonal structure is denied by many experimental facts obtained by X-ray, neutron, NMR measurements, and so on, the interface at the border of the grains, which does not have space inversion symmetry, can be considered. CeRh_2Si_2 is known to easily have mosaic of the crystal. The sample used for present measurement has $\text{RRR} \sim 11$ that is not so high in CeRh_2Si_2 . Then, the present sample might also have some mosaic. However, it is difficult to give a plausible explanation for the experimental fact that the ME effects have non-zero value. In general, it is expected that the mosaic distribution in this system is isotropic or has in-plane/out-of-plane anisotropy with respect to [001] axis or growing direction of the crystal. In each case, if the ME effects occur at the boundary of grains, they would compensate to each other in total. It requires a gimmick to have non-zero ΔM .

d) Domain wall of magnetic structure

Magnetic structure below T_{N1} has symmetrically equivalent two structures. One is the structure denoted by $\mathbf{q} = (0.5, 0.5, 0)$ and the other is the one denoted by $\mathbf{q} = (-0.5, 0.5, 0)$. Since ferroic arrangement of moments appears at the domain boundary, it also could be magnetoelectrically active. The fact that the peak intensities for each $\mathbf{q}$ vectors are almost the same implies that many domains exist in a sample. The same discussion about the compensation can be applied again. Thus, domains should have a kind of superstructure or be aligned by i along to $[100]$.

Consequently, on the basis of the previous reports about magnetic structure of CeRh_2Si_2 , the ME effects observed in this system is very difficult to understand as a bulk property or the surface effect. The interface of magnetic or crystallographic domains can be a cause, although it needs a gimmick to explain it.

3.7 Conclusion

We have performed magnetization measurements under electric current in the collinear antiferromagnetic compound CeRh_2Si_2 . We have revealed that the application of electric currents parallel to $[100]$ induces static magnetization of $\sim 6 \times 10^{-11} \mu\text{B}/\text{Ce}$ per unit current density, in the current direction of $[001]$ only between T_{N1} and T_{N2} . In the present understandings about the physical properties of CeRh_2Si_2 and the ME effects on metallic systems, it cannot be explained as the bulk ME effects. The present results indicate that many antiferromagnet might have the ME effects. The magnetization measurement under electric currents on other antiferromagnetic systems should be helpful to understand the required conditions of the ME effects. Regarding CeRh_2Si_2 , microscopic measurements under electric currents are desired to gain a better understanding of the origin of this phenomenon.

4 An improvement on the techniques for the growth of single crystals of UNi₄B

4.1 Introduction

The goal of another project mentioned in Section 3-1 is to recheck magnetic and crystal structure of UNi₄B by means of neutron diffraction measurement. Czochralski method is usually used to grow a single crystalline sample of UNi₄B [31]. In general, to find an appropriate method and good conditions to grow the single crystalline sample of a specific system is quite hard. Thus, we usually follow the method reported in the papers. However, UNi₄B, which is the system having distorted triangular lattice, is known that the mosaic easily appears during the growing process. Such a sample does not suit to the neutron-scattering measurements. Thus, some improvements on the crystal-growth techniques for this particular compound are required.

Since it is prohibited to handle U materials in the neutron-source facility J-PARC in Tokai, Japan, this project has been being pursued as a collaboration with Prof. S. Süllow's group (TU Braunschweig, Germany) and Prof. V. Sechovský's group (Charles University, Czech Republic). I took charge of the single crystal growth of UNi₄¹¹B. Since ¹⁰B is a good neutron absorber, the sample is necessary to be enriched by ¹¹B. After a dozen trials, we have succeeded in growing an enriched single-crystalline sample by floating zone method. Moreover, we have found better conditions to grow a single-crystalline sample with less mosaic. The revealed conditions are applicable for other intermetallic compounds such as UAu₂Si₂, UIrSi₃, and so on, which we actually grew and provided for other projects.

In this chapter, the crystal-growth procedure, the crystal-growth conditions, the sample evaluation, and the problem of the procedure will be presented.

4.2 The experimental details

The single crystal growth of UNi_4B was performed twice by a Bridgman method, 3 times by a Czochralski method, and 9 times by a floating zone method. A polycrystalline sample was put in BN crucible and sealed in Mo capsule for the Bridgman method. It is heated with an induction furnace up to $\sim 1200^\circ\text{C}$ in the vacuum. A tri-arc furnace was used for Czochralski method. A tungsten rod was used as the seed. The polycrystalline rod-shape sample for the floating zone method was prepared by using a mono-arc furnace. First, a button shape sample was prepared in a mono-arc furnace. Then, shuttered polycrystalline pieces were melt again to make a rod. A rod is cut into two pieces by using the wire saw. An optical furnace was used for growing the single-crystalline sample. The trial was repeated by slightly changing the growing conditions, especially the rotation and translation speed of the rod and molten.

Typically, U element was purified by a solid-state electron-transport method and the purity of Ni and B is 4N and 2N5, respectively.

The grown samples were mainly evaluated by using Laue photography (Laue) and energy dispersive X-ray spectrometry (EDX). Mosaicity and crystal structure can be checked by Laue. The existence of impurity phase, its distribution and composition, and the homogeneity and composition of the bulk can be checked by EDX. Since the existence of B is hard to be detected by the EDX apparatus we used, the composition ratio of only U and Ni was checked, basically. X-ray powder diffraction measurement was performed on only a few samples, because it does not suit to a check for the amount of impurity on a system forming unidentified structure, and we know that the intensity is not enough to distinguish the crystal structure.

4.3 Results

4.3.1 Bridgman method

Single-crystalline samples could not be obtained by this procedure. Figure 4-1 shows an EDX image obtained by a Back Scattered Electron (BSE) mode. This mode is sensitive to the composition of materials near the surface. The color difference indicates the composition difference. The lighter area has heavier elements. The light gray area that occupies the most part of the surface has the ratio of U:Ni $\sim$ 1:4. However, since U attacks BN crucible, all the sample obtained by this procedure has Ni-rich region with the rate of U:Ni $\sim$ 1:7 (the darker gray area in the light gray). It might be difficult to obtain homogenous sample with appropriate composition by this procedure.

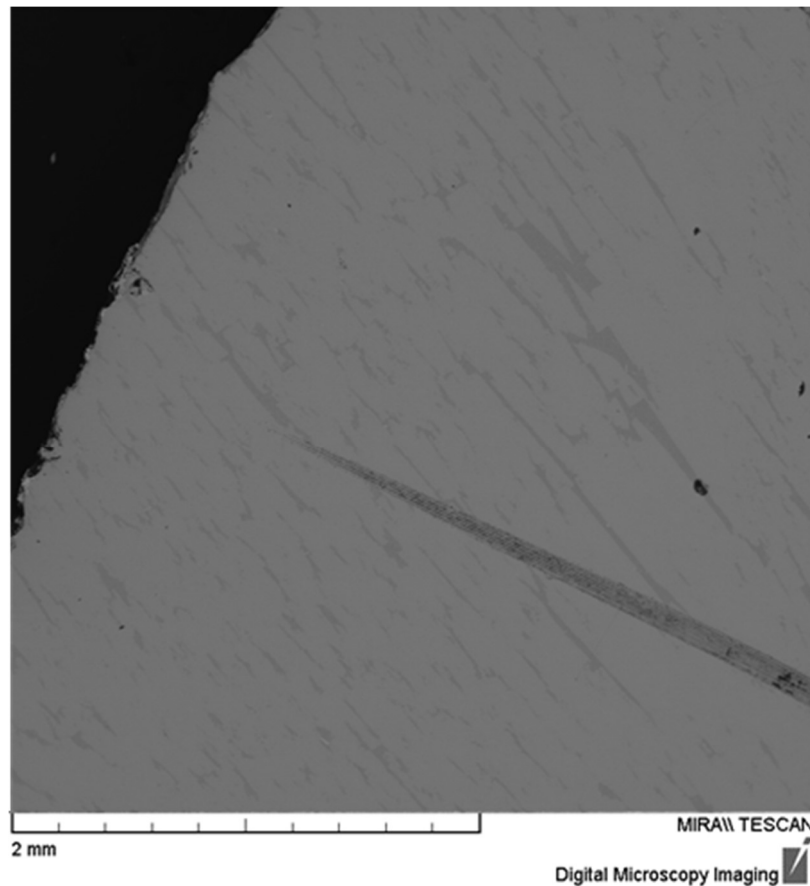


Fig. 4-1. An EDX image obtained by BSE mode on UNi₄B sample grown by Bridgman method. Magnification is $\times 50$.

4.3.2 Czochralski method

One of the good conditions to grow a single crystalline sample of $\text{UNi}_4^{11}\text{B}$ has been reported in a previous report [31]. They suggest that 0 rpm crucible rotation, 5 mm/h seed translation, and 12 rpm seed rotation are the best in their trials.

We have followed this condition at first, then realized it is no good. In our case, slower rotation and translation speed yielded a better quality of the sample. However, the sample grown by Czochralski method seems good only near “the neck” while the hard mosaic or twins are visible in the part far from “the neck” (Fig. 4-2).

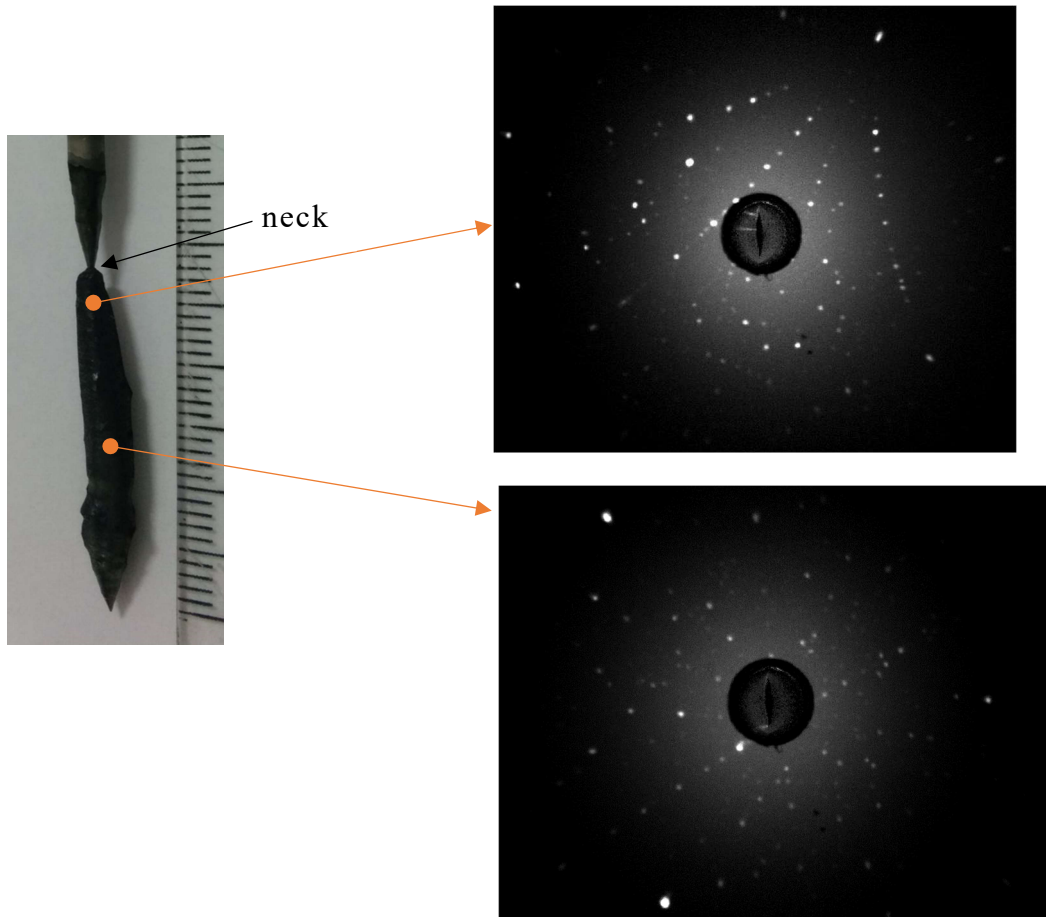


Fig. 4-2. An appearance of UNi_4B sample grown by Czochralski method (left panel). A Laue image obtained on each surface indicated by arrows in the photo (right panels).

4.3.3 Floating zone method

From the above trials, we realized that growing the sample *statically* should give better result. However, it is very difficult to keep the condition constant by the Czochralski method. For instance, the temperature of the molten can be controlled by the distance between the electrodes and the molten. It changes gradually during the growing process, since the amount of molten decreases because it is pulled up from the crucible. We should change the positions of the electrodes gradually all along, otherwise growing conditions will be changed.

Judging from the above results and considerations, we concentrated on the trial of the single crystal growth by the floating zone method. The temperature of the molten is controlled by the heater power, the focus position of heater lamps, the translation speed, the diameter of the polycrystalline rod, and the flowing rate of an inert gas (Ar) in chamber. Since all of them can be fixed during the growing process, it is very easy to achieve the constant condition. The best result was obtained in the conditions of 1 mm/h translation and 0 rpm rod rotation.

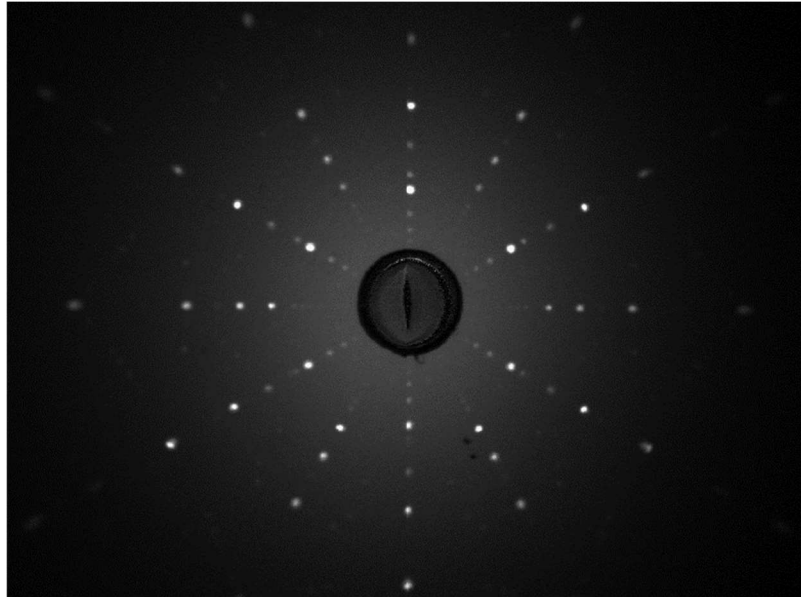


Fig. 4-3. A Laue image of a UNi₄B single crystal grown by floating zone method. The *c* axis is oriented.

As can be seen in Fig. 4-3, the crystal has obviously less mosaic than the sample grown by Czochralski method. The size of the obtained single-crystalline piece is roughly $\phi 4 \text{ mm} \times 10 \text{ mm}$, which is large enough for the usage in almost all of the measurements. In actual, the ultrasound measurements, which usually require rectangular parallelepiped samples with a dimension of $\sim 1 \text{ mm}^3$ or larger, are now going on with applying pulsed magnetic fields.

4.3.3.1 Carbon contamination

We found a problem that is specific for the system containing U and Ni, by checking EDX of the sample. Figure 4-4 shows an EDX image of UNi₄B grown by the floating zone method in BSE mode. It has certain amount of an impurity phase which has the ratio of U:Ni ~ 1:1 and C-rich, while the most part has the ratio of U:Ni ~ 1:4. In our best knowledge, there are no reports on the binary or ternary systems with an atomic ratio of U:Ni = 1:1. Thus, this impurity phase might have a composition of UNiC_x(B_y). The contamination of C is considered to come from the U element we used. C exists in U when we bought it and C cannot be removed by the SSE purifying process.

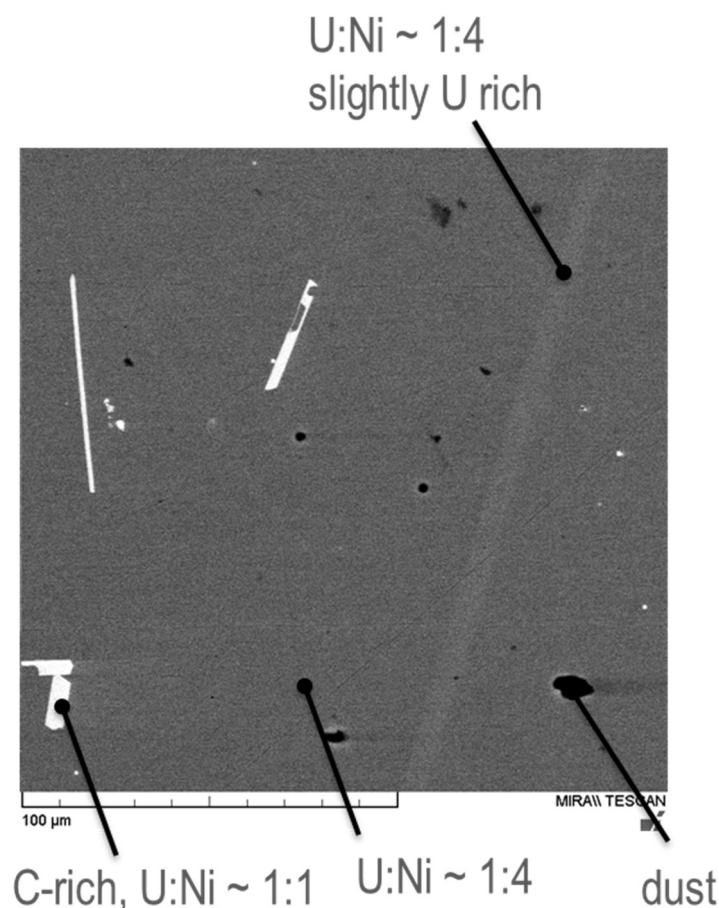


Fig. 4-4. An EDX image obtained by BSE mode on UNi₄B single crystal grown by floating zone method. Magnification is $\times 1k$.

From the magnetization measurements (not shown), we see that this impurity is non-magnetic down to 2 K. Thus, the contamination of C will not crucially influence most of the measurements.

In addition to the above, one more feature caused by C is found on the enriched $\text{UNi}_4^{11}\text{B}$. Figure 4-5 shows an EDX image obtained by BSE mode on $\text{UNi}_4^{11}\text{B}$ and EDX energy spectra for the bulk (gray) and the line (light gray). As can be seen, the intensity corresponding to C (B) is larger in the line (bulk) while the intensities of U and Ni are almost the same. The intensity of the EDX spectrum corresponds to the composition ratio. It indicates that some part of ^{11}B is replaced by C. We should evaluate the effects of the replacement to the physical properties before using it for the neutron-diffraction measurements.

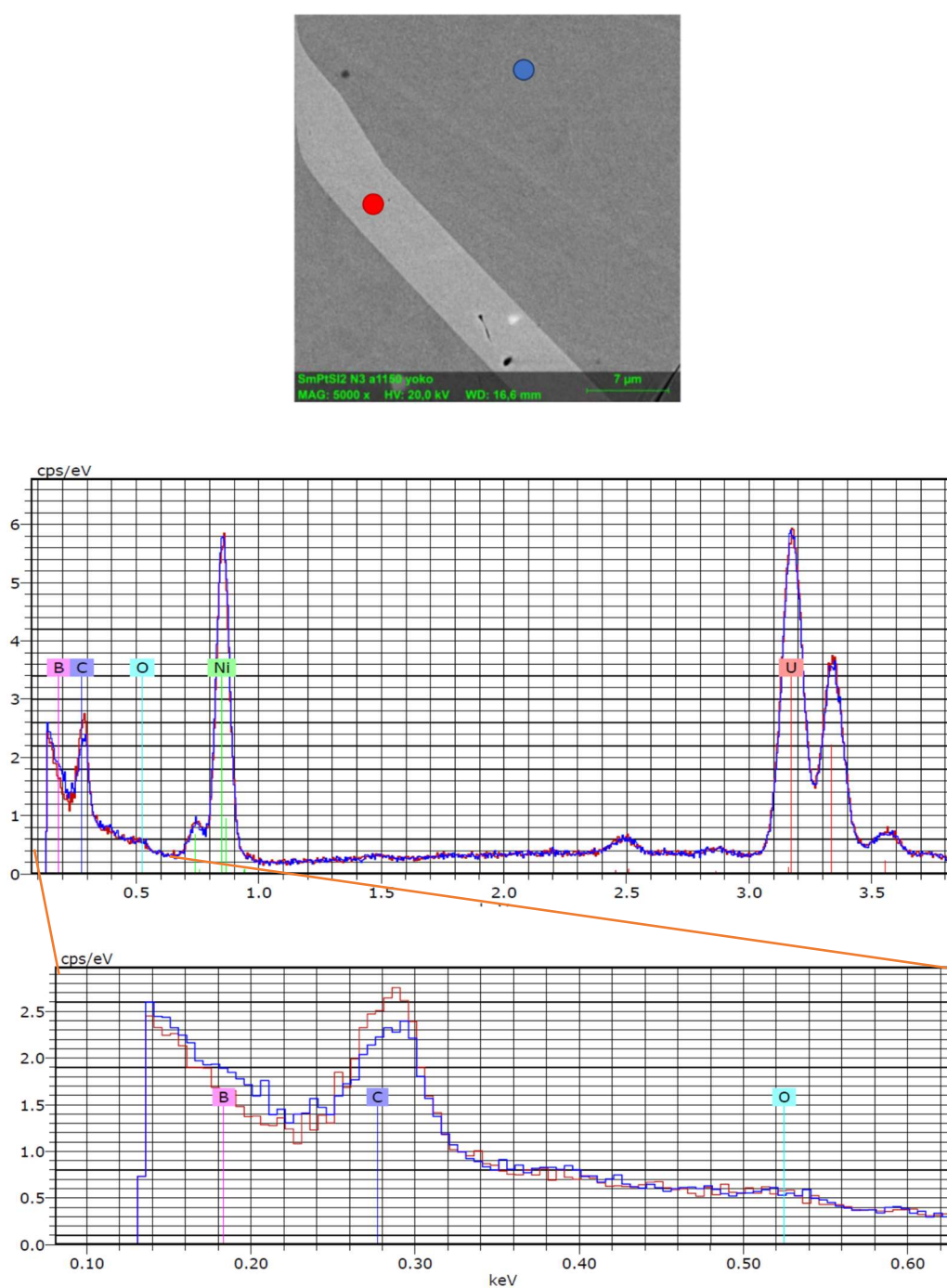


Fig. 4-5. An EDX image obtained by BSE mode and EDX spectrum on a $\text{UNi}_4^{11}\text{B}$ single crystal grown by floating zone method. Magnification is $\times 5\text{k}$. Blue(Red) data were taken at blue(red) circle in the EDX image.

4.4 application for other compounds

Setting apart from the problem of C contamination, let us now introduce the application of the present technique for other compounds. Though this project was pursued, keeping mainly UNi_4B in our mind, we realized that the same technique works quite well for other systems. Hereafter, I would like to introduce the results of UAu_2Si_2 . Since UAu_2Si_2 is incongruent melting, it was annealed in the muffle furnace up to 1000°C for 1 week before the single crystal growth. Figure 4-6 shows a Laue image on UAu_2Si_2 . Though small distortion exists in each spot, the spots are rather sharp and bright indicating the good crystallographic quality of the crystal.



Fig. 4-6. A Laue image of UAu_2Si_2 single crystal grown by floating zone method. The c axis is oriented.

Figure 4-7 shows an EDX image obtained by BSE mode on UAu_2Si_2 . There is no impurity phase except for a tiny U oxide in the center of the image. The homogeneity of the sample can be confirmed. I would like to mention that this result indicates that C contamination is negligible for UAu_2Si_2 .

Since this is the first success of the growth of a UAu_2Si_2 single-crystalline sample larger than 1 mm^3 dimensions, this sample has been used for ultrasound and neutron-diffraction measurements [32].

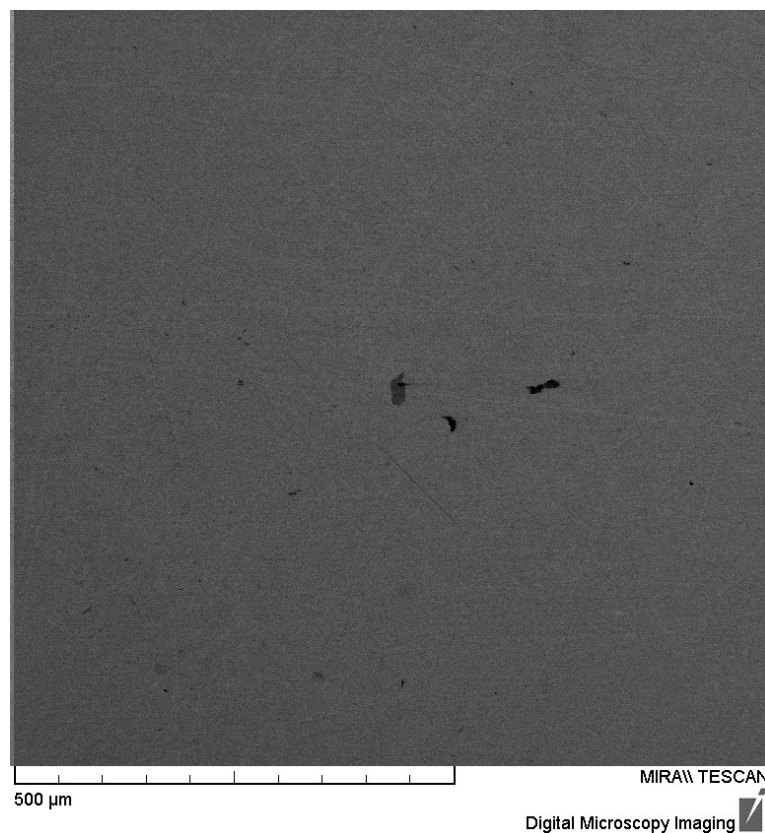


Fig. 4-4. An EDX image obtained by BSE mode on UAu_2Si_2 single crystal grown by floating zone method. Magnification is $\times 200$.

4.5 Conclusion

We have succeeded in growing single-crystalline sample of $\text{UNi}_4^{11}\text{B}$, and revealed that the floating zone melting is a powerful method to grow large single crystalline samples. Regarding $\text{UNi}_4^{11}\text{B}$, we still need to check carefully the effects of a carbide impurity phase. On the other hand, the growing condition I optimized is applicable for various compounds. This procedure has been successfully used on UAu_2Si_2 , UIrSi_3 , NiMnGa_2 , and so on, contributing to the development of international collaborations. The present work is helpful in the measurements which require large single crystalline samples. In actual, ultrasound and neutron diffraction measurements on UNi_4B and UAu_2Si_2 are now ongoing.

5 Magnetic phase diagram of UNi₄B

5.1 Previous works

UNi₄B was discovered in 1978 [33]. It had once been researched intensively by S. Mentink in 1990's as a candidate material for heavy fermion frustrated system. They mainly focused on a complicated vortex-like magnetic structure that appears in zero magnetic field below $T_N = 20.4$ K. They performed not only macroscopic but also microscopic measurements on single crystalline sample until they found a heavy-fermion-like upturn of specific heat below 5 K is just a foot of another order at $T^* = 0.3$ K [22]. Present understandings about the physical properties of UNi₄B are summarized below.

UNi₄B forms orthorhombic structure with the symmetry $Cmcm$ (D_{4h}^{17} , No.63) where U-ions form distorted triangular lattice [18]. It has once been believed that the structure is CeCo₄B-type hexagonal which has perfect triangular lattice of U ions [21]. S. Mentink *et al.* suggested possible subtle positional changes of B ions that lower the 6-fold symmetry at U-ion site to 2-fold from superreflections on their neutron diffraction measurement [34]. Y. Haga *et al.* corrected these pictures by high resolution X-ray diffraction measurement on single crystalline sample [18].

Neutron scattering study suggests that UNi₄B exhibits an AF order at $T_N = 20.4$ K [19]. In this ordered state, only 2/3 of U ions participate the ordering and the magnetic moments lies in c plane, forming a periodic array of vortex-like magnetic clusters in the shape of a hexagon. This magnetic structure is however still suspicious because the calculation was given based on hexagonal crystal structure. It was revealed by magnetization measurement under magnetic field up to 50 T that the system presents several spin reorientations (SR) by in-plane magnetic field. UNi₄B shows several transitions by applying field in plane. The transition fields are $B_2 = 8.2$ T, $B_2 = 11.7$ T, and $B_0 = 19.8$ for $T = 4.2$ K and B along $[2\bar{1}10]$. For field along $[01\bar{1}0]$, they are $B_1 = 9.3$ T and $B_0 = 18.6$ T for $T = 4.2$ K [35]. The spin structures of these

spin reorientation phases are not known. UNi₄B shows another order at $T^* = 0.3$ K for zero magnetic field [22]. Specific heat measurement under magnetic field is the only report that provides the data below 0.3 K. Thus, the order parameter of T^* is not known, while it is expected that 1/3 of paramagnetic U ions might order antiferromagnetically at T^* .

5.2 The aim of this work

As seen in Chapter. 1, it is suspected that toroidal moment which is a kind of odd-parity multipole appears below T_N and contributes the physical properties of UNi₄B. Thus, it should be useful to investigate again the physical properties of UNi₄B in terms of the multipoles. In order to obtain further information about the contribution of multipole to not only the ferroic toroidal ordered phase but also spin reorientation phases and another order below T^* on UNi₄B, magnetization, electric resistivity, dilatometry, specific heat measurements are performed on single crystalline sample of UNi₄B grown by floating zone method.

5.3 Experimental details

Magnetization measurements along $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ were mainly performed by vibrating sample magnetometer (VSM) equipped in PPMS with 14 T superconducting (SC) magnet (PPMS14, Quantum Design inc.). In order to investigate low field anomaly observed in in-plane magnetization, PPMS with 9 T SC magnet and MPMS with 7 T magnet were also used. Electric resistivity and longitudinal magnetoresistance measurements along $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ were performed using an AC transport option of PPMS14. Au wires are contacted to the sample by spot welding. Dilatometry and longitudinal magnetostriction measurements along $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ were performed using a miniature capacitance dilatometer [36] implemented in PPMS14. Specific heat measurements field along $[2\bar{1}\bar{1}0]$ were performed by PPMS14.

All the sample were cut into appropriate rectangular parallelepiped shapes by wire saw from a single crystalline ingot and then polished well. A brick shaped sample was used for both of magnetization and dilatometry measurement. The conditions of the measurements are summarized in the tables put on the top of each subsection.

5.4 Specific heat

Table. 5-1 The summary of measurement conditions. B direction is $[2\bar{1}10]$.

Sample Mass (mg)	Magnetic Field B (T)	Temperature T (K)
9.14	0	2 – 300
	1, 5, 10, 14	2 – 30

Specific heat measurements in magnetic field were performed only for $B \parallel [2\bar{1}10]$. The sole reason of the lack of data is machine-time scheduling of PPMS.

Figure 5-1 shows temperature dependence of heat capacity C divided by temperature T as a function of T for zero magnetic field. C/T shows gradual increase by decreasing T . It shows round maximum around 90 K, then decrease rapidly. C/T shows λ -type anomaly that corresponds to phase transition from paramagnetic to AF at $T_N = 20$ K. T_N is 0.4 K lower than previous reports. The ordering temperature may be affected by carbon contamination. In actual, it is known that carbon contamination suppresses AF order of UNi_4B [37]. C/T increase by decreasing T below ~ 6 K. It is reported previously that this upturn is a foot of another order at $T^* = 0.3$ K. All the features are either qualitatively or quantitatively consistent with previous C/T data of UNi_4B . In other words, any indication of the impurity phase except for carbon is not observed.

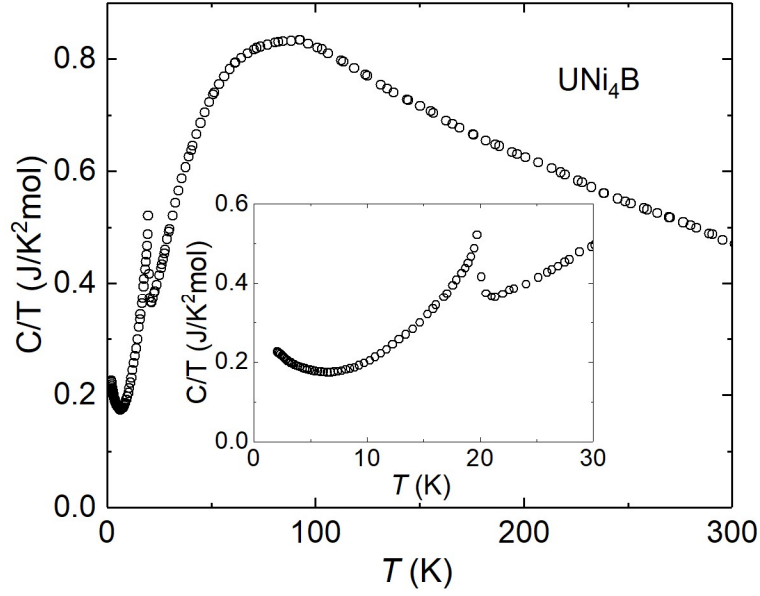


Fig. 5-1 C/T versus T in the temperature range 2 – 300 K and (inset) 2 – 30 K.

Note that this data may contain a part of specific heat of apiezon grease because the known heat capacity data of grease was used by normalizing to subtract its contribution. Specific heat of apiezon grease in present measurement is measured only few temperature points for normalization. We realized that the normalized data cannot reproduce the data obtained in present data of grease indicating subtraction cannot exclude all the contribution of apiezon grease to C . A weak saturating feature of C/T around 3 K might be a contribution of apiezon. This feature also can be seen in the data measured applying magnetic field (Fig. 5-2).

Figure 5-2 shows T dependence of C/T below 30 K for magnetic field $B = 0, 1, 5, 10$, and 14 T applied along $[2\bar{1}\bar{1}0]$. T_N decreases by increasing field. The winding behavior of C/T below 10 K for $B = 10$ and 14 T might correspond to the phase transition between two spin reorientation phases. However, it is difficult to determine the ordering temperatures from this data that may have additional winding feature caused by specific heat of apiezon grease. Ordering temperatures T_N are plotted into BT phase diagram which will be shown later. The height of a jump at T_N is strongly suppressed between 5 and 10 T. This suppression may correspond to the switching of the ordered phase from AF to spin reorientation.

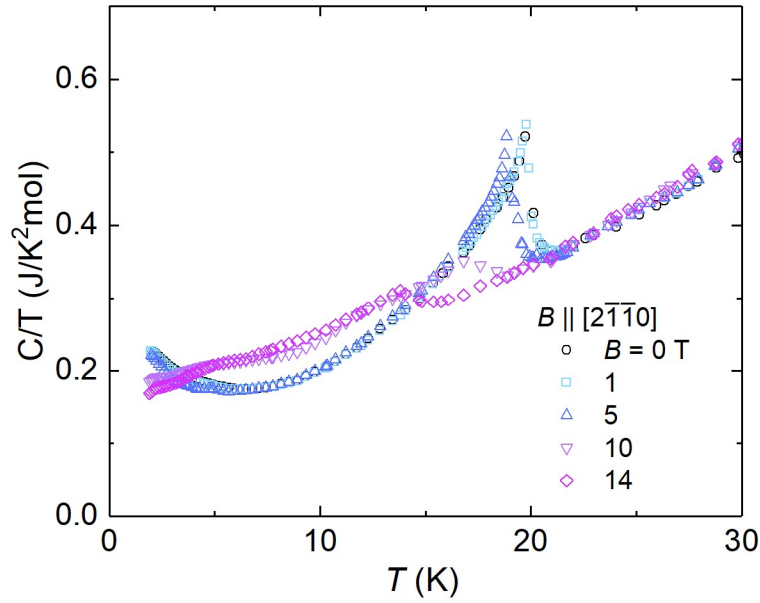


Fig. 5-2 C/T versus T for $B = 0, 1, 5, 10$, and 14 T.

5.5 Magnetization

Table. 5-2 The summary of measurement conditions. Sample mass is 80.412 mg.

Orientation	Magnetic field B (T)	Temperature T (K)	Note
$B \parallel [2\bar{1}\bar{1}0]$	1	2 – 300	PPMS14, VSM
	0.1, 1, 3, 5, 7, 8, 9, 10, 11, 14	2 – 50	
	0 – 14	4, 10, 15, 21	
$B \parallel [01\bar{1}0]$	0.5	2 – 300	
	0.1, 0.3, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14	0 – 30	
	0 – 14	1.9, 4, 7, 12, 18, 21	
$B \parallel [2\bar{1}\bar{1}0], [01\bar{1}0]$	-5 – 5	1.9, 4, 7, 10, 12, 15, 18, 21	PPMS14
$B \parallel [2\bar{1}\bar{1}0]$	-5 – 5	18	MPMS
$B \parallel [0001]$	0 – 14	1.9, 21	PPMS14
	1, 14	1.9 – 300	

5.5.1 Paramagnetic phase

Figure 5-3 shows temperature dependence of magnetization M divided by magnetic field H for $B = 1$ T, applied along $[2\bar{1}\bar{1}0]$ (●) and $[0001]$ (+), respectively. The inset is its inverse, H/M . A cusp anomaly corresponds to AF order is found around $T_N = 20$ K. This value is slightly lower than previous papers as mentioned in previous section. M/H for $B \parallel [2\bar{1}\bar{1}0]$ down to 50 K can be fit by modified Curie-Weiss law; $\chi = \chi_0 + C/(T - \Theta)$, where C indicates Curie constant, Θ Curie temperature, and χ_0 constant parameter, which is mostly caused by Van-Vleck paramagnetism or Pauli paramagnetic impurity, respectively. The obtained parameters are $\Theta = -28.8$ K and effective moment $\mu_{\text{eff}} = 2.52 \mu_B$, respectively. These values are well consistent with previous paper [38] (Table 5-2). Almost same parameters are obtained by M/H for $B = 0.5$ T applied along $[01\bar{1}0]$. On the other hand, M/H for $B \parallel [0001]$ shows weaker temperature dependence and does not follow a modified CW law.

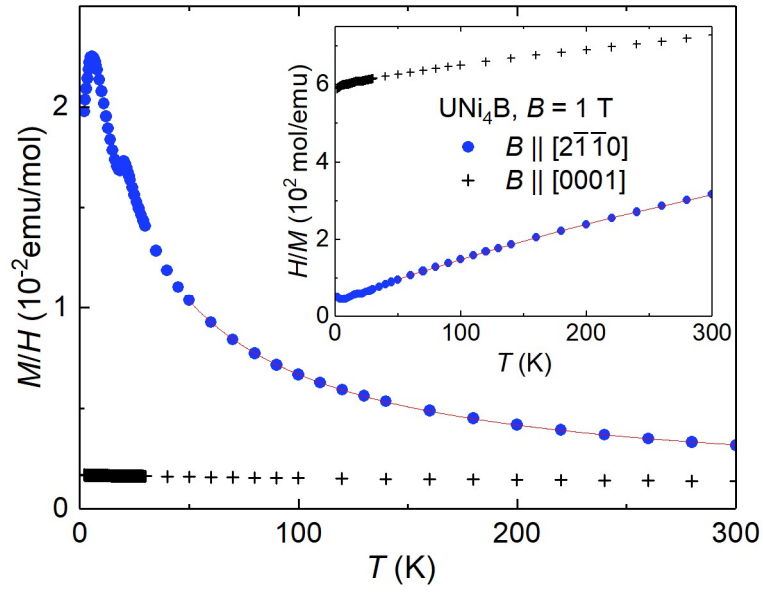


Fig. 5-3 M/H and (the inset) the inverse of M/H for $B = 1$ T applied along $[2\bar{1}\bar{1}0]$ and $[0001]$, respectively.

Tab. 5-3 The obtained parameters of modified Curie-Weiss law. “Present” is obtained from Fig. 5-1. “Hokkaido Univ.” is the data measured in our group (not shown).

Identity	Orientation	Θ [K]	$\mu_{\text{eff}} [\mu_B]$	Note
Present	$B \parallel [2\bar{1}\bar{1}0]$	-28.8	2.52	
	$B \parallel [01\bar{1}0]$	-28.1	2.47	
Hokkaido Univ.	$B \parallel [2\bar{1}\bar{1}0]$	-29.2	2.52	
S.A.M. Mentink [39]	in plane	-64.8	2.90	CW law
A. Oyamada [38]	$B \parallel [2\bar{1}\bar{1}0]$	-28	2.48	

5.5.2 M for $B \parallel [2\bar{1}\bar{1}0]$

Figure 5-4 shows T dependence of M/H for several B values applied along $[2\bar{1}\bar{1}0]$ in Field Cool (FC) and Zero Field Cool (ZFC) conditions. T_N shifts to lower temperature and an upturn of M/H observed for $B = 0.1$ T below T_N is suppressed by increasing B . These features are well consistent with previous report given by S.A.M Mentink *et al.* [39] In addition, we newly found hysteretic behavior in ordered phase. It can be seen in wide region below T_N for $B = 0.1$ T. That region shifts to lower temperature by increasing field and cannot be observed at $B = 5$ T. This region is put in BT phase diagram as contour plot (Fig. 5-8).

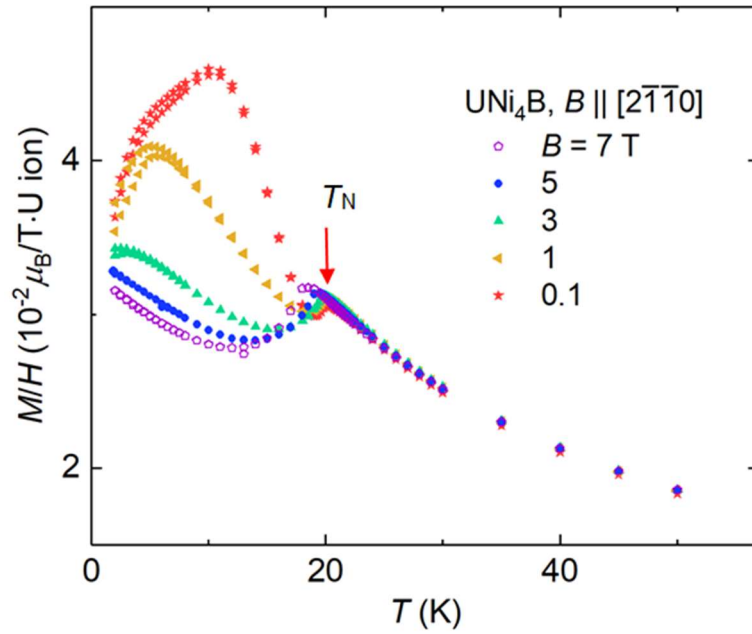


Fig. 5-3 M/H for $B = 0.1, 1, 3, 5$, and 7 T applied along $[2\bar{1}\bar{1}0]$. FC and CC data are plotted by same marker.

Figure 5-4 shows T dependence of M for B over than 8 T. M for B lower than 7 T shown in Fig. 5-3 is presented in Fig 5-4 by gray circles for comparison. Step like anomalies that corresponds to the phase transitions from AF to spin reorientation SR1 (T_1 , yellow arrows, $\downarrow$) and from SR1 to SR2 (T_2 , orange-colored arrows, $\downarrow$) can be seen in $B = 8, 9$, and 10 T, in addition to T_N (red arrows, $\downarrow$). The region of SR1 phase is smaller than previous paper [35]. This discrepancy may be caused by sample quality, which will be discussed later.

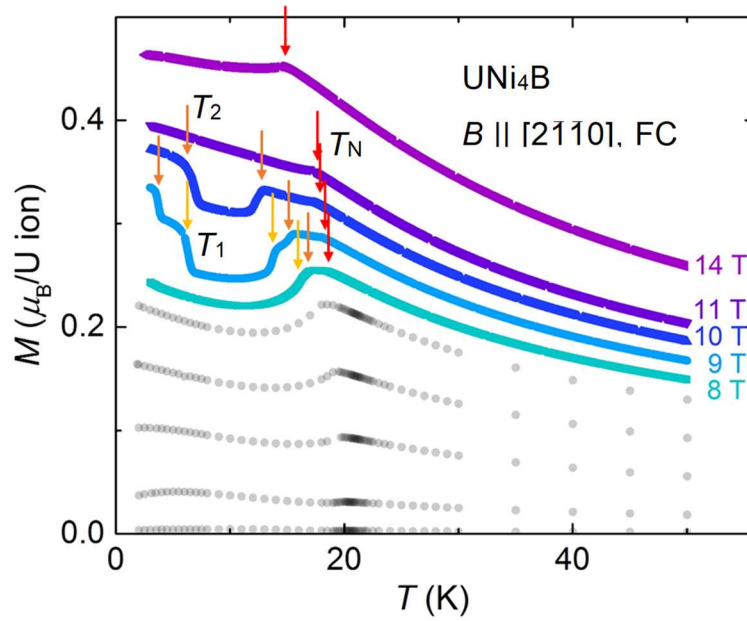


Fig. 5-4 M for $B = 8, 9, 10, 11$, and 14 T applied along $[2\bar{1}\bar{1}0]$. The measurement was performed in FC condition. The ordering temperatures are separated into T_1 , T_2 and T_N indicated by orange-colored, yellow, and red arrows by taking BT phase diagram into account.

B dependence of M for B along $[2\bar{1}\bar{1}0]$ measured at $T = 4, 10, 15, 18,$ and 21 K is shown in Fig. 5-5. Metamagnetic like features B_1 and B_2 that corresponds to T_1 and T_2 are found around 8 T. Hysteretic behavior is observed only at $T = 4$ K. As one can realize, hysteresis loop has asymmetric shape; the data observed by decreasing B shows sharper step. The ordering field is determined as a peak of the first derivative of M with respect to B (Fig. 5-6). By checking carefully dM/dB vs B , we found that UNi_4B has additional metamagnetic-like feature B_3 in low field (the inset of Fig. 5-6).

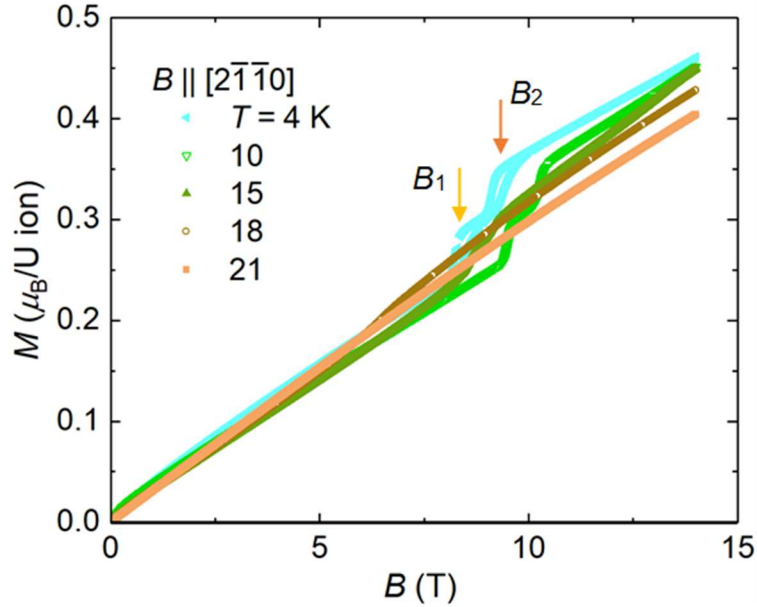


Fig. 5-5 M vs $B \parallel [2\bar{1}\bar{1}0]$ for $T = 4, 10, 15, 18$ and 21 K. One metamagnetic like behavior observed in lower B corresponds to T_1 is named B_1 . The other one is named B_2 .

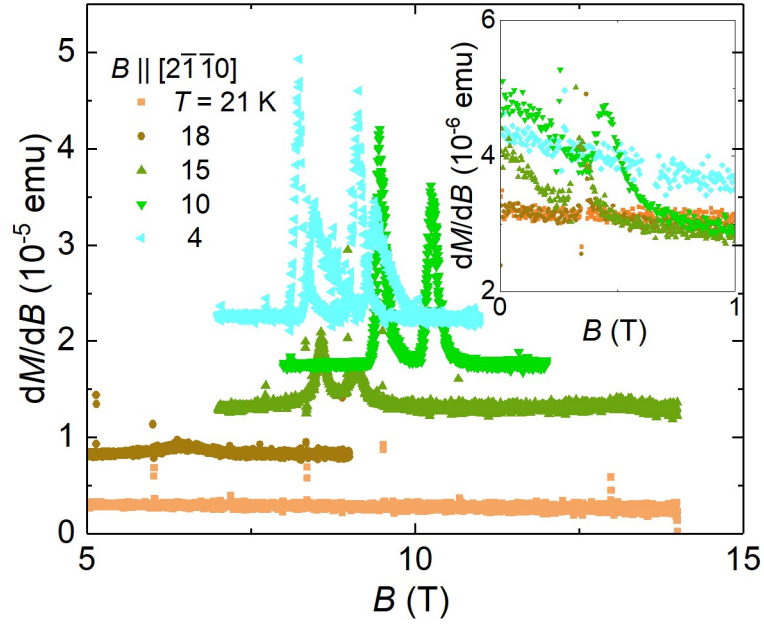


Fig. 5-6 dM/dB vs $B \parallel [2\bar{1}\bar{1}0]$ for $T = 4, 10, 15, 18$ and 21 K. Data are shifted vertically. The peak position corresponds to metamagnetic like step of M . Four peaks can be seen at $T = 4$ K since it has hysteretic feature. The inset shows first derivative of initial curve vs B for $B < 1$ T. Another peak named B_3 is observed around 0.5 T below T_N .

Figure 5-7 shows B dependence of M for $B \parallel [2\bar{1}\bar{1}0]$ up to 1 T. Initial magnetization curves and data measured in B decreasing condition are presented. Metamagnetic feature observed in initial curve around $B_3 \sim 0.4$ T below T_N is obscure on magnetization measured in B decreasing condition while suppression of M around 0 T becomes sharp. This low field anomaly may originate from frustration caused by slightly distorted magnetic and crystal structure or a kind of magnetic domain. This behavior also could correspond to hysteretic behavior observed in temperature dependence.

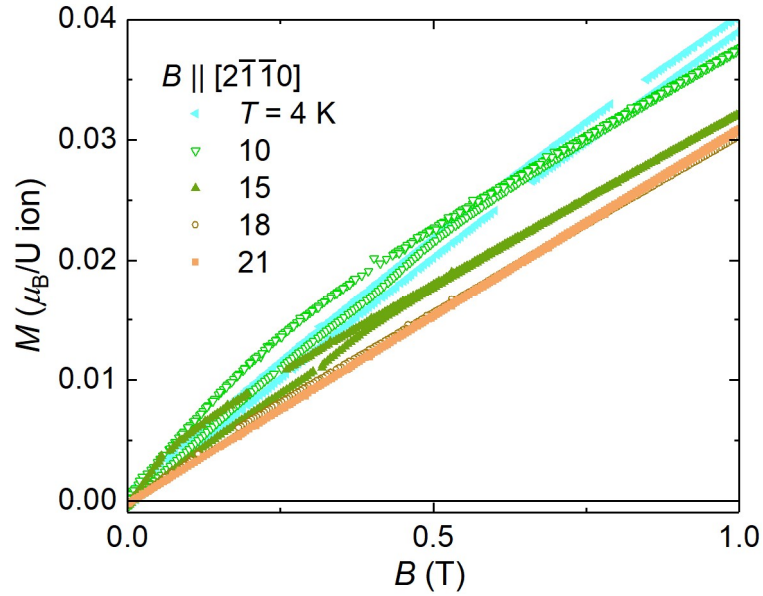


Fig. 5-7 M vs $B \parallel [2\bar{1}\bar{1}0]$ for $T = 4, 10, 15, 18$ and 21 K and $B < 1$ T. Initial magnetization curve and data measured in B decreasing condition are shown.

The anomalies obtained from T and B dependence of M are summarized in BT phase diagram as shown in Fig. 5-8. ΔM is the height of a hysteric behavior observed in T dependence of M . It is defined as $\Delta M = M(\text{FC}) - M(\text{ZFC})$. The phase diagram is overlaid by a contour plot of ΔM . ΔM becomes larger when B and/or T decreases. It is known that there is another phase below $T^* \sim 0.3$ K and $B < 4$ T. The development of in-plane U-U exchange interaction, which is expected to be a cause of another order, may also drive ΔM . The obtained phase diagram is almost consistent with the previously reported one [35] except for the size of the region of SR1. The phase boundaries of ordered phase are well identified in the present diagram. It allows us to estimate the entropy change by the phase transitions from AF to SR1 and SR1 to SR2. It will be mentioned in Section 5-5-4.

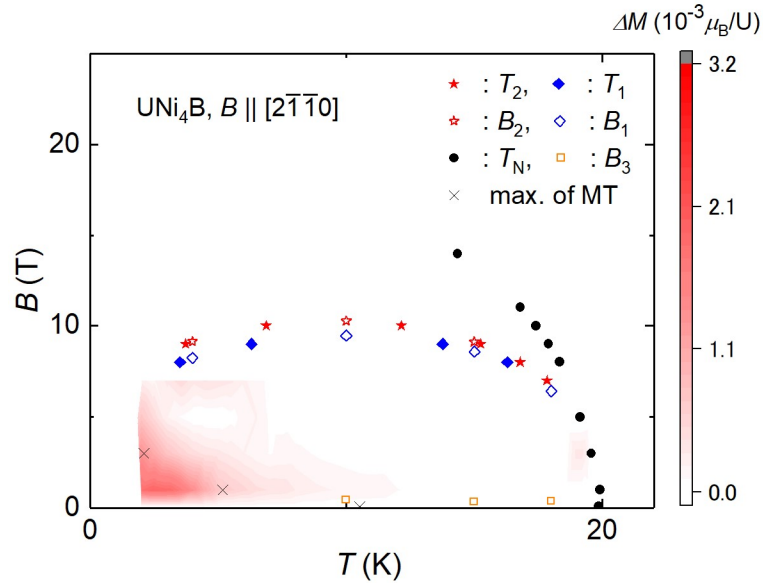


Fig. 5-8 BT phase diagram of UNi_4B for $B \parallel [2\bar{1}\bar{1}0]$. ΔM is the height of hysteresis observed in T dependence of M . The open (closed) symbols are obtained from field (temperature) scan, respectively.

5.5.3 M for $B \parallel [01\bar{1}0]$

Temperature and field dependence of magnetization for $B \parallel [01\bar{1}0]$ is similar to one for $B \parallel [2\bar{1}\bar{1}0]$. Thus, I would like to mention mainly the difference between magnetization for $B \parallel [2\bar{1}\bar{1}0]$ and $[01\bar{1}0]$ by showing the results of magnetization measurement for $B \parallel [01\bar{1}0]$.

Figure 5-9 and 5-10 show T dependence of M/H for B no more than 5 T and M for B . M/H for $B = 0.1$ T has slightly smaller value than other field, indicating that the sample used for the measurement has small amount of PM impurity. The hysteretic behavior observed below T_N is more or less same with the one observed for $B \parallel [2\bar{1}\bar{1}0]$. Thanks to finer spacing of magnetic field than $B \parallel [2\bar{1}\bar{1}0]$, we can see the detailed feature of it. The largest hysteresis is achieved at $B = 0.3$ T. It is suppressed by increasing B . However, it still remains at $B = 4$ T.

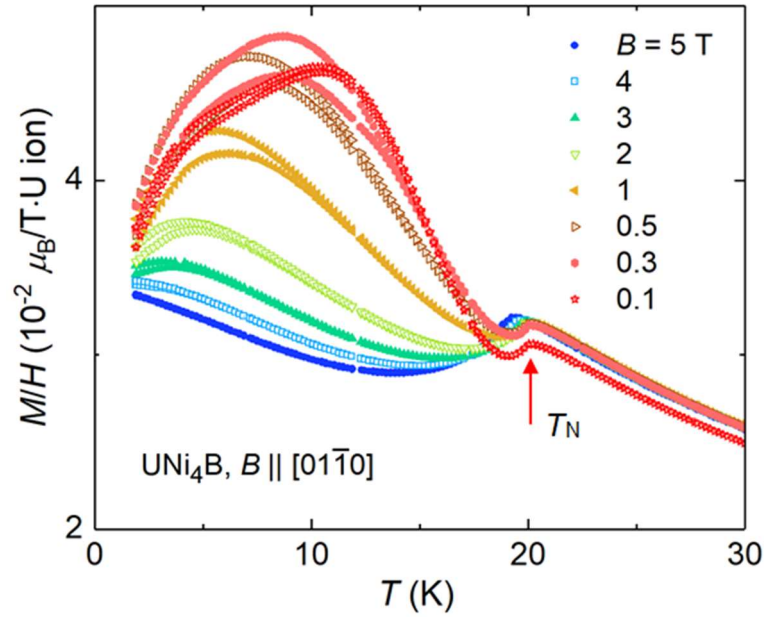


Fig. 5-9 T dependence of M/H for $B = 0.1, 0.3, 0.5, 1, 2, 3, 4$, and 5 T ($\parallel [01\bar{1}0]$). A red arrow indicates transition temperature T_N from PM to AF. The data measured under FC and CC conditions are plotted as same symbol.

The ordering temperatures are decided as the peak of first derivative of M with respect to T (not shown). As can be seen in Fig. 5-10, T_2 indicated by orange-colored arrows are more obscure than those for $B \parallel [2\bar{1}\bar{1}0]$. One can find small difference between the data measured under FC and CC condition at 7 T below T_1 . The data measured under FC condition are smaller than another. This strange feature might be caused by the metastable state of transition from AF to SR1. It should be checked carefully again. MT for $B = 13$ and 14 T seems to have another transition just below T_N . It might imply another ordered phase in high field.

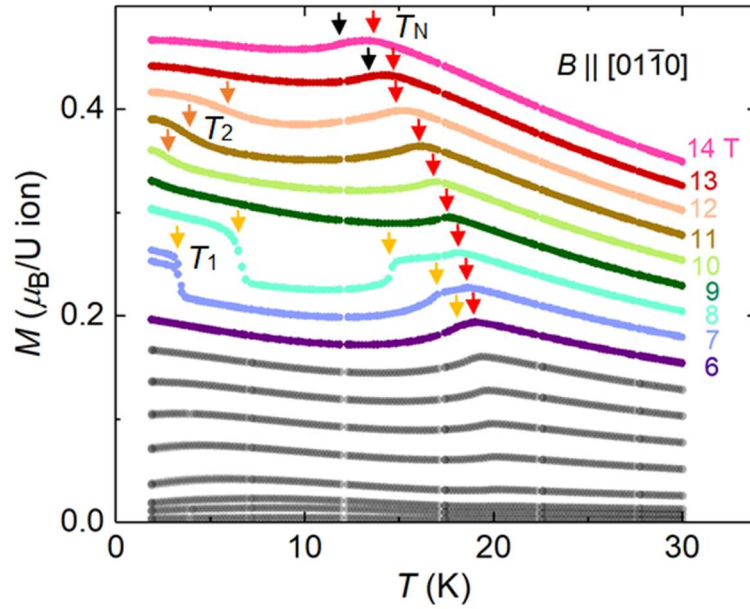


Fig. 5-10 T dependence of M for $B = 6 - 14$ T ($\parallel [01\bar{1}0]$). The red, orange-colored, and yellow arrows indicate transition temperature T_2 , T_1 , and T_N , respectively. The data measured under FC and CC conditions are plotted as same symbol. The data shown in Fig. 5-9 are plotted as gray circle.

Figure 5-11 shows magnetization curve for $B \parallel [01\bar{1}0]$. The data are shifted vertically. A hysteresis loop B_1 that corresponds to a transition from AF to AR1 is strongly enhanced by cooling while step like anomaly B_2 that corresponds to the ordering from SR1 to SR2 becomes obscure. These behaviors are well consistent with previous report given by S.A.M mentink *et al.* [35]. B_1 is decided as the midpoint of hysteresis with respect to B .

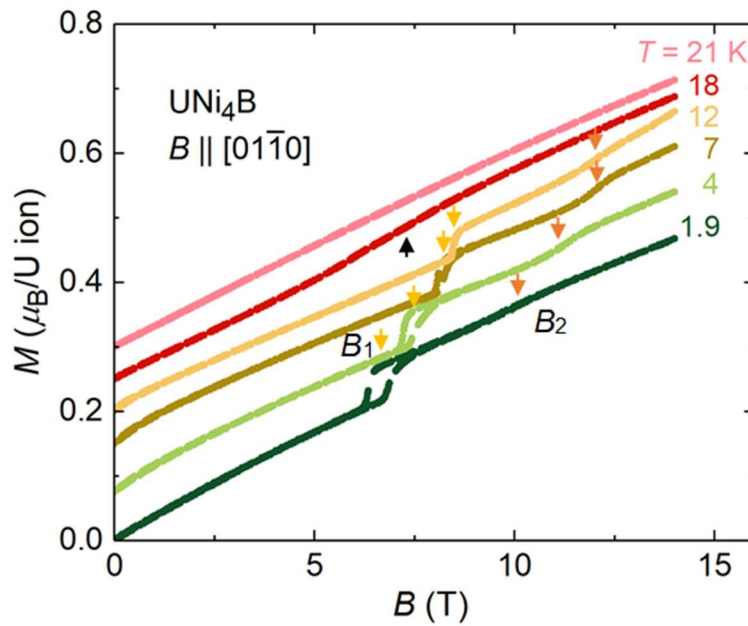


Fig. 5-11 B dependence of M for $T = 1.9, 4, 7, 12, 18,$ and 21 K. The orange-colored and yellow arrows are transition field B_2 and B_1 , respectively.

The ordering temperatures and magnetic fields and the height of hysteresis ΔM are summarized into a BT phase diagram shown in Fig. 5-12. Most significant difference between the diagrams for $B \parallel [2\bar{1}\bar{1}0]$ and $[01\bar{1}0]$ is the size of SR1 phase. This feature seems to be inconsistent with previous phase diagram [35]. SR1 phase is larger for the field parallel to $[01\bar{1}0]$ in our results while SR1 is not observed by S.A.M. Mentink for this direction. One might think that a mistake on the sample direction as a cause of this discrepancy. However, magnetization data for $B \parallel [01\bar{1}0]$ shown in ref. 35 are measured at only $T = 1.9$ and 4.2 K. B_2 at low temperature is obscure in the present data. Thus, we think lower quality of their sample hindered another transition at B_2 in the previous result.

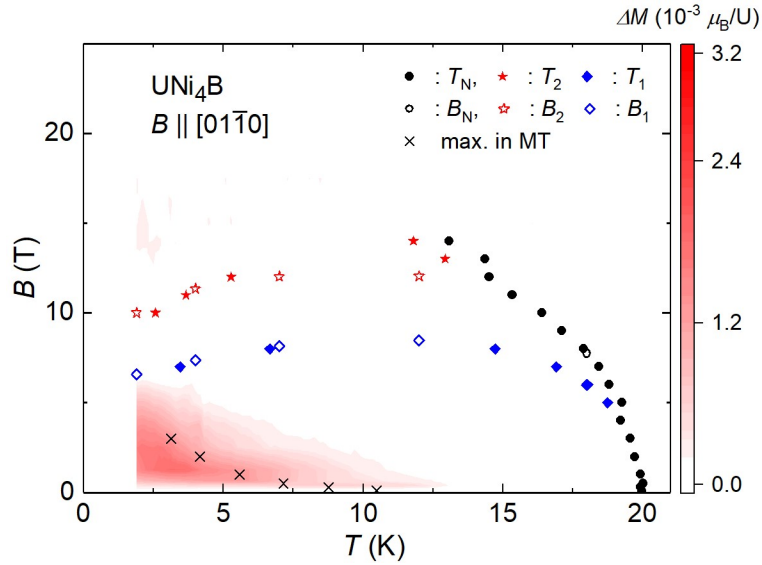


Fig. 5-12 BT phase diagram of UNi_4B for $B \parallel [01\bar{1}0]$. ΔM is the height of hysteresis observed in T dependence of M . The open (closed) symbols are obtained from field (temperature) scan, respectively.

5.5.4 Entropy change

Let us now calculate the entropy change. If a transition is the first order, it must preserve Clapeyron-Clausius equation; $dS = dM \cdot (dB/dT)$, where dS denotes entropy change, dM the height of a step of M at the transition, and dB/dT the slope of phase line in BT phase diagram.

Figure 5-13 shows temperature and magnetic field dependence of entropy change ΔS . ΔS is a function of T and B . The condition of B is put in the graph as a text. ΔS at a transition from AF to SR1 increases by decreasing temperature. Since the phase-boundary line shows convex curve, ΔS becomes zero around 10 K. Thus, each phase of AF, SR1, and SR2 has the same energy at that condition. Below ~ 10 K, ΔS starts increasing again by decreasing T . ΔS suddenly decreases below 5 K for $B \parallel [2110]$, while it remain large for $B \parallel [0110]$. A complex two-humped shape of ΔS implies the existence of a competition of the couplings around 10 K. The quenching of the one-dimensional ferromagnetic excitations of the 1D chain of PM U ions that suggested by S.A.M Mentink [35] can be considered as one of the possible cause. The other possibility is the competition between multipole degrees of freedom: especially, magnetic dipole and electric quadrupole. An ultrasound measurement performed recently in our group [40] have revealed the existence of an electric quadrupole degree of freedom that has Γ_5 symmetry below T_N .

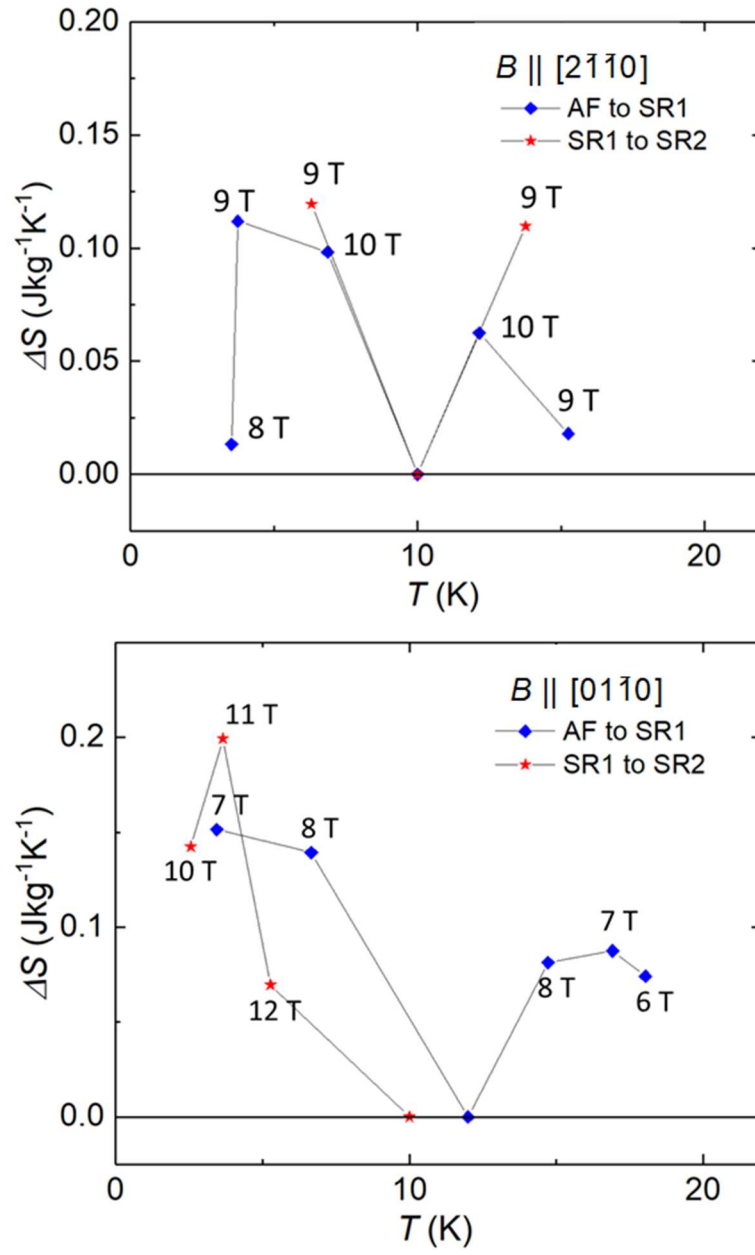


Fig. 5-13 Temperature dependence of entropy change ΔS for (top) $B \parallel [2110]$ and (bottom) $B \parallel [0110]$. Blue rhombuses denote ΔS for a transition from AF to SR1. Red stars are ones for from SR1 to SR2.

5.5.5 Low field anomaly induced by in-plane magnetic field

As mentioned in Section 5.5.3, magnetization curve shows sharp drop around 0 T. By checking the data carefully, we realized that this anomaly is also a metamagnetic-like one forming a strange hysteresis. Figure 5-14 shows magnetization curve around 0 T for $B \parallel [21\bar{1}0]$ measured at $T = 18$ K on PPMS with a 14 T SC magnet (PPMS14) and MPMS with a 7 T magnet. There is a small hysteresis below 0.5 T. In addition, the data measured in the condition of B increasing (M_{inc}) got larger than one measured in the condition of B decreasing (M_{dec}) below ~ 0.1 T.

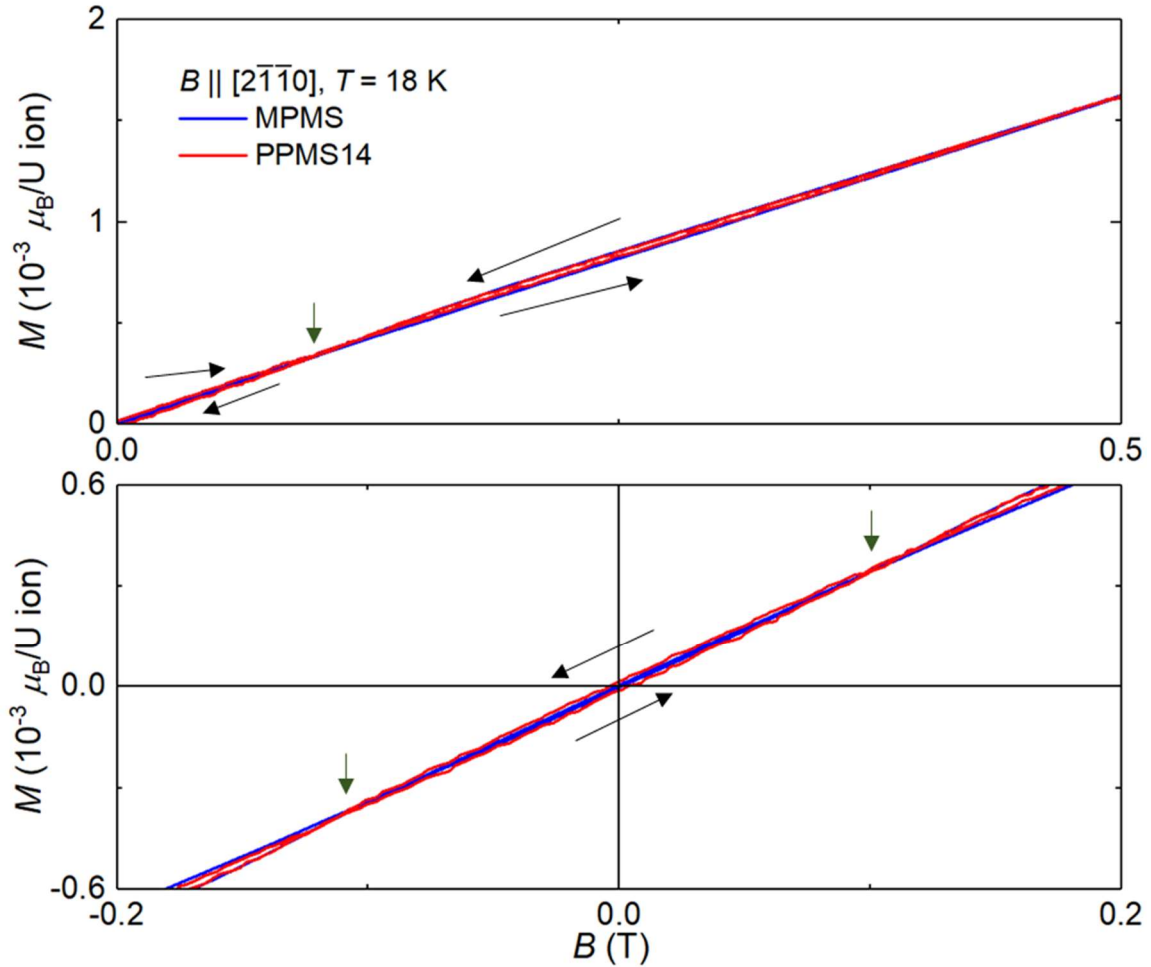


Fig. 5-14 M vs H for $B \parallel [21\bar{1}0]$ and $|B| < 0.5$ T. Black arrows denote scanning direction of measurement. Green arrows are crossing field of M_{inc} and M_{dec} .

It is known that SC magnet has the remanent magnetic field when one sets field 0 T after applying magnetic field [41]. Figure 5-15 shows the typical remnant magnetic field (field error) when one sets 0 T after applying arbitrary magnetic field (applied magnetic field). Thus, the actual field becomes ~ 120 G when one sets field 0 T after applying 14 T on 14 T SC magnet. It can be a cause of reversed hysteretic behavior if the system has ferroic behavior without hysteresis. Thus, we performed same measurement on MPMS that has a 7 T SC magnet (Figs. 5-14, 16, and 17). It is obvious that a reversed hysteresis significantly exists though the height of hysteresis is changed slightly by changing the measuring system.

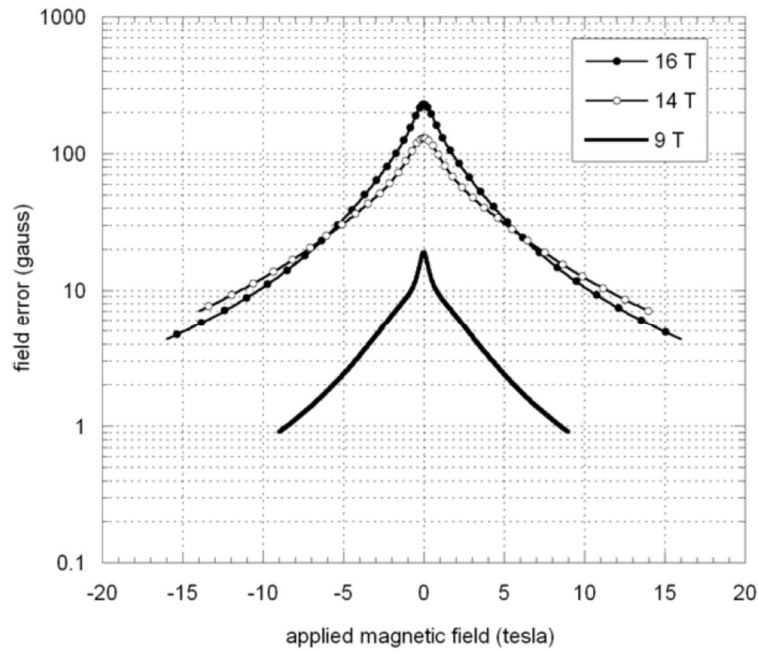


Fig. 5-15 The typical remnant magnetic field (field error) when one set field 0 after applying arbitrary magnetic field (applied magnetic field). 9 T, 14 T and 16 T denotes the highest field of the SC magnets [41].

Figure 5-16 shows B dependence of the first derivative of M with respect to B for $B \parallel [2110]$ at $T = 18$ K. One can find that there are two peaks in each data and the position of the peaks is independent of the measurement system. The latter confirms that this result is intrinsic. Surprisingly, larger peak is observed in negative (positive) field in dM_{inc}/dB (dM_{dec}/dB). It can be understood that, for instance, the magnetic moment starts flipping before field across 0 T. The competition between spin-orbit interaction and spin-spin interaction may lead such curious behavior observed in low field. Figure 5-17 shows the height of hysteresis calculated by $M_{\text{dec}} - M_{\text{inc}}$. This graph helps as to see the sign flipping of hysteresis in low field. The sharp change corresponds to the peak of dM/dB in Fig. 5-16. As you can see, data obtained on PPMS14 do not become 0 when the hysteresis loop gets closed. It might be caused by the measurement procedure: a continuous measurement with sweeping field.

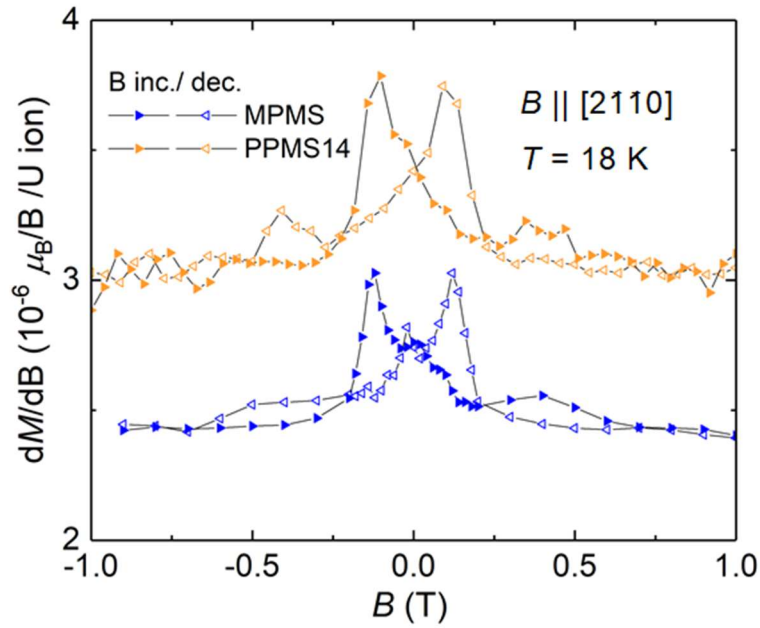


Fig. 5-16 dM/dB vs B for $B \parallel [2110]$ at $T = 18$ K measured on MPMS and PPMS14. The peaks indicate the change of the slope in M - B . In other words, they indicate the existence of metamagnetic like behavior on that field.

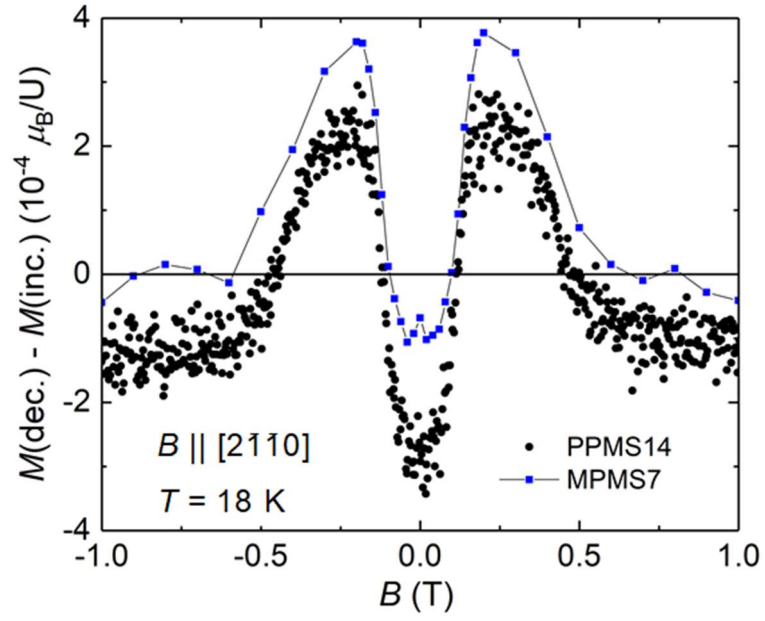


Fig. 5-17 B dependence of the difference of M_{dec} and M_{inc} . It shows the size and the sign of hysteresis. At each field point they show dramatic change corresponds metamagnetic like behavior of M . It is pronounced in Fig. 5-16.

Same measurements performed at other temperatures and for B along [0110]. Figure 5-18 shows B dependence of dM/dB for $B \parallel [0110]$ at $T = 1.9 - 21$ K. Larger peaks observed in “negative” field at 18 K are strongly enhanced and across 0 T between 15 and 12 K. It becomes obscure by decreasing temperature, and almost disappears ~ 7 K. The measurements performed for $B \parallel [2110]$ and analyzed in the same manner. Finally, we got phase diagrams for field $B \parallel [2110]$ and [0110] shown in Fig. 5-19. Phase diagrams are more or less the same except for additional anomaly observed in initial curve for $B \parallel [0110]$. As stated above, this behavior may correspond to small in-plane distortion of UNi_4B . It should be investigated by other physical properties. However, earnestly to say, we could not find any indication of low-field anomaly by magnetoresistance and magnetostriction because of the low accuracy of the measurements.

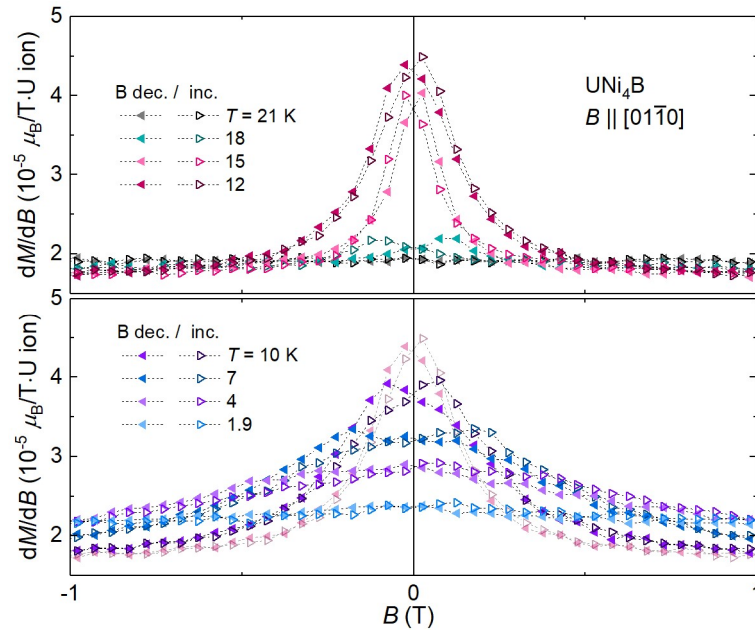


Fig. 5-18 dM/dB vs B for $B \parallel [0110]$ at $T = 1.9, 4, 7, 10, 12, 15, 18$ and 21 K. The symbol of $\blacktriangleleft$ ($\blacktriangleright$) shows dM_{dec}/dB (dM_{inc}/dB). Peak position of larger peak shifts by decreasing temperature and across 0 T between 15 and 12 K.

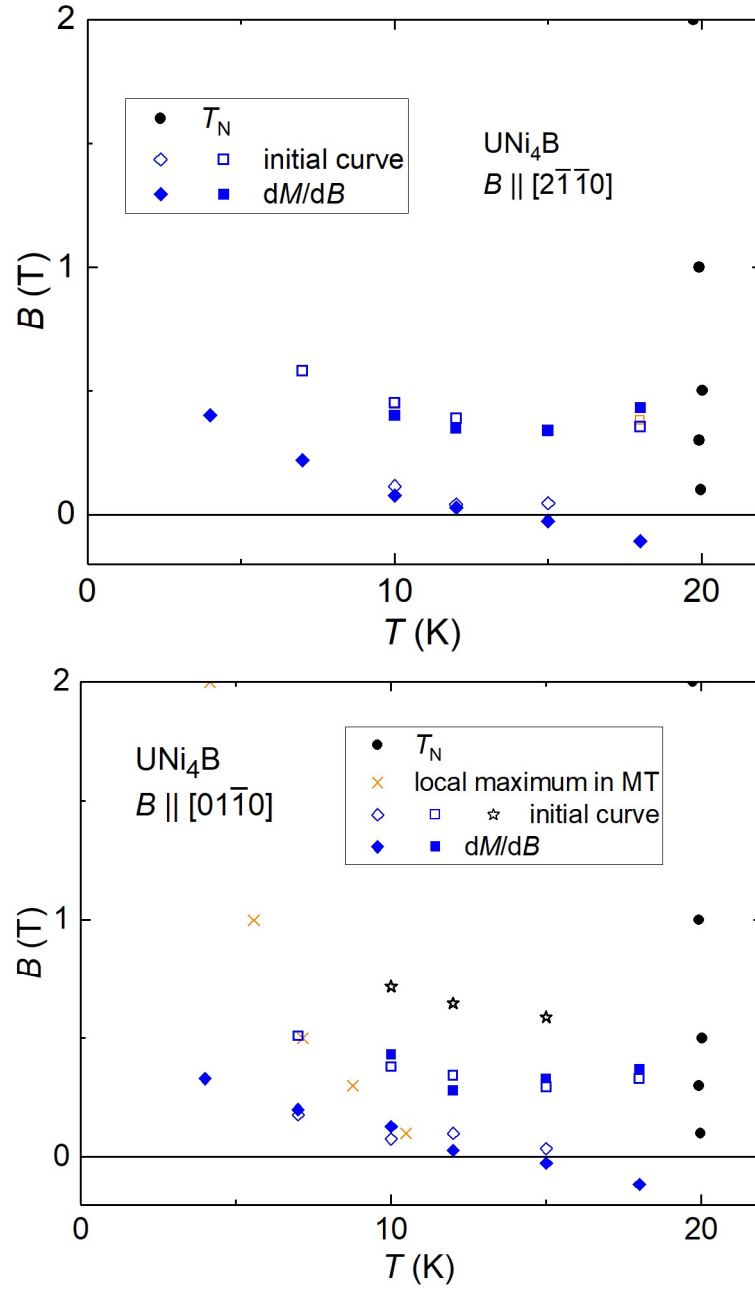


Fig. 5-19 BT phase diagram of UNi_4B for $B \parallel$ (top) $[2110]$ and (bottom) $[0110]$ for $B < 2$ T. Closed symbols are obtained from dM_{inc}/dB . Open symbols are obtained from initial curve.

5.5.6 M for $B \parallel [0001]$

$[0001]$ axis of UNi_4B is known to be magnetic hard axis. It is consistent with our measurement. A strange upturn of M/H is observed in a temperature scan (Fig. 5-20). We think that this is an error of the measurement because there is nothing corresponding to it in the observed magnetization curve.

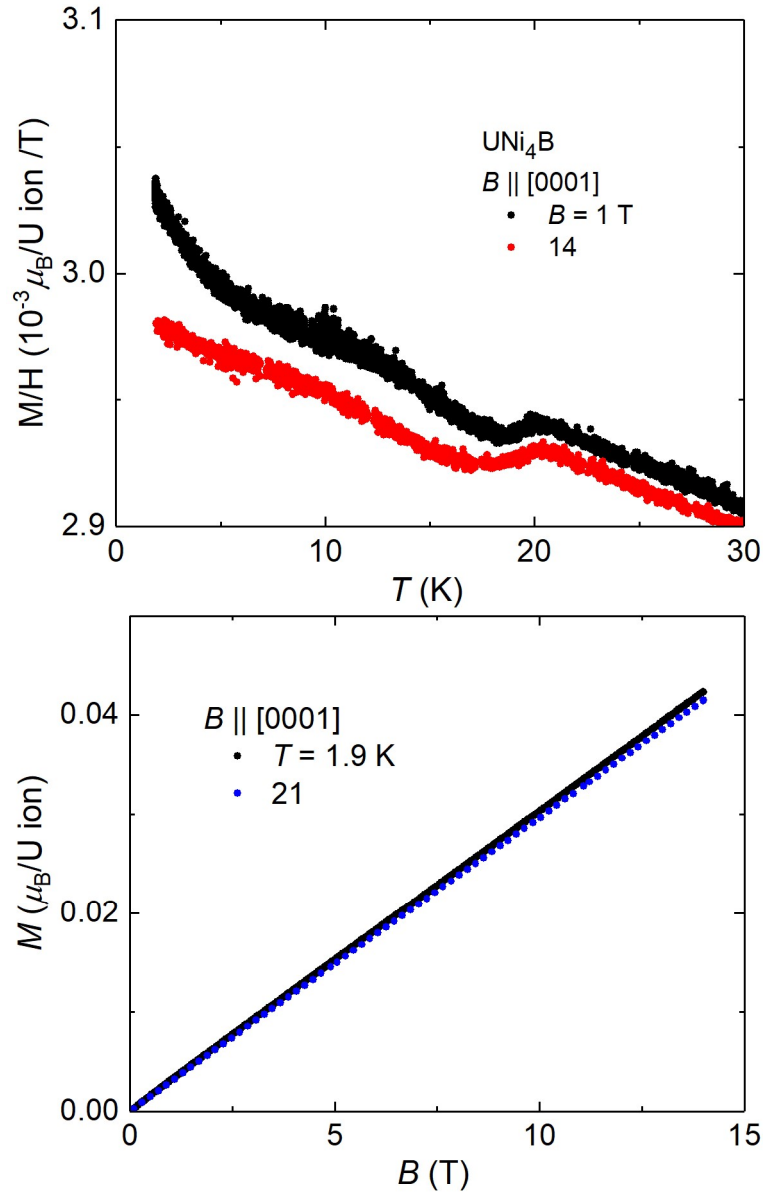


Fig. 5-20 (top) M/H vs T and (bottom) M vs B for $B \parallel [0001]$. The system is not affected by B ($\parallel [0001]$) of 14 T.

5.6 Resistivity and magnetoresistance

In order to compare with magnetization data, longitudinal magnetic field is chosen for magnetoresistance measurement. The rectangular parallel-piped sample with well polished surfaces are prepared for each geometry.

Table. 5-4 The summary of measurement conditions. Au is used for the electric contact.

Size (mm ³)	Orientation	B (T)	T (K)
$2.77 \times 0.41 \times 0.56$	$I \parallel B \parallel [2110]$	0, 0.1, 0.3, 0.5, 1, 3, 5, 7, 10, 14	0 – 30
		-1 – 14	1.9, 4, 7, 10, 12, 15, 18, 21
$0.38 \times 0.54 \times 3.0$	$I \parallel B \parallel [0110]$	0, 1, 3, 5, 7, 10, 14	0 – 50
		-1 – 14	1.9, 4, 7, 10, 12, 15, 18, 21
$0.28 \times 0.25 \times 2.0$	$I \parallel B \parallel [0001]$	0, 3, 7, 10, 14	0 – 50

5.6.1 Magnetoresistance for longitudinal magnetic field $B \parallel [2110]$

Figure 5-21 shows temperature dependence of resistivity ρ for I and $B \parallel [2110]$. The measurements performed in both of FC and ZFC conditions below 3 T. Any hysteretic behavior was observed in the accuracy of the measurement. In-plane resistivity shows a Kondo-effect-like increase by decreasing temperature in the whole temperature region. It shows a jump at $T_N \sim 20$ K for $B = 0$ T. It is similar to the temperature dependence caused by gap opening at Fermi surface due to AF order. This is well consistent with the previous results and the present understandings of magnetic structure. ρ decrease by increasing B . jump anomaly is changed to kink anomaly in the high fields of 10 and 14 T. The anomaly point indicated by arrows in Fig. 5-21 is determined from the first derivative of ρ .

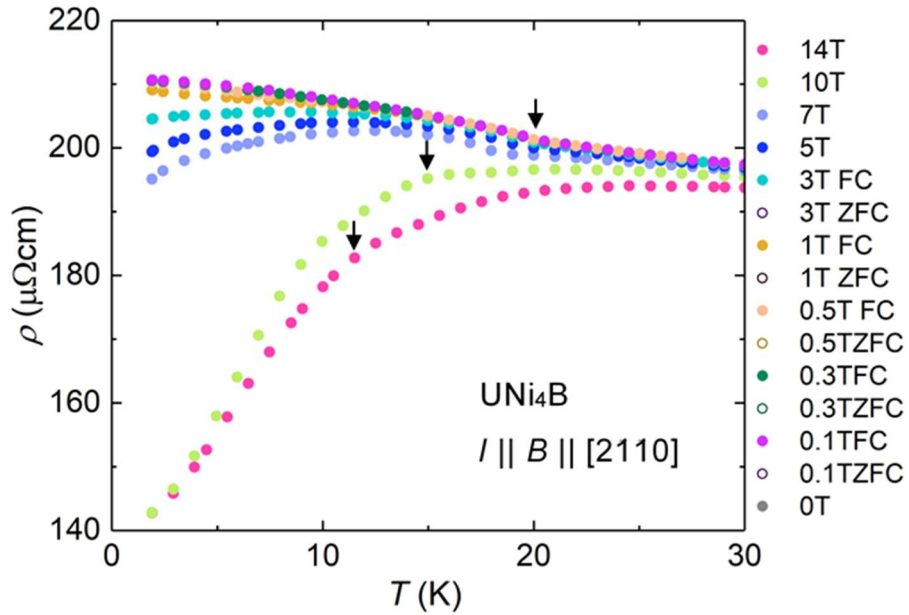


Fig. 5-21 Resistivity ρ vs T for $I \parallel B \parallel [2110]$ at $B = 0, 0.1, 0.3, 0.5, 1, 3, 5, 7, 10$, and 14 T. FC and ZFC data are indicated by closed and open symbols, respectively. Black arrows are ordering temperatures T_N .

Figure 5-22 shows field dependence of magnetoresistance measured for $I \parallel B \parallel [2110]$ at $T = 1.9, 4, 7, 10, 12, 15, 18$, and 21 K. ρ decreases with increasing B . We first performed the measurement at 1.9 K from -14 T to 14 T to check its symmetric behavior with respect to B , and to confirm the measurement condition itself. Then, the measurement was performed from -1 to 14 T. A shoulder-shaped structure is found below $B = 0.5$ T and $T = 10$ K. It might correspond to a low field anomaly observed in M . However, we could not find appropriate anomaly point. The inflection points are plotted in the obtained phase diagram. Another feature is a steep drop of ρ with large hysteresis around 8 T. Taking BT phase diagram obtained by magnetization measurement into account, it is expected that this steep drop is composed of two steps corresponding B_1 and B_2 observed in magnetization curve. It becomes one in the present measurement because of rough steps of magnetic field. The ordering fields are also determined from the first derivative.

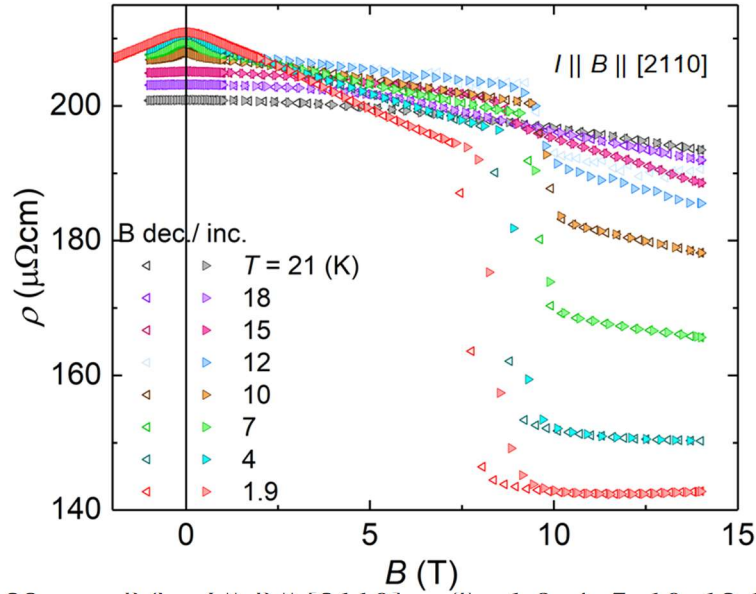


Fig. 5-22 ρ vs B for $I \parallel B \parallel [2110]$ at $T = 1.9, 4, 7, 10, 12, 15, 18$, and 21 K. The symbols of $\blacktriangleleft$ ($\blacktriangleright$) indicates magnetoresistance measured in the condition of B decreasing, ρ_{dec} (B increasing, ρ_{inc}), respectively.

The anomalies obtained from Figs. 5-21 and 22 are summarized in BT phase diagram shown in Fig. 5-23. Hysteretic behavior emerges below 7 T after the slope of the phase-boundary line becomes positive. One can find that inflection point of ρ does not coincide with hysteretic behavior or low-field metamagnetic like behavior of M , by comparing with Fig. 5-8. I would like to note again that anomalies indicated by blue diamond probably include two anomalies of B_1 and B_2 (see also Fig. 5-8)

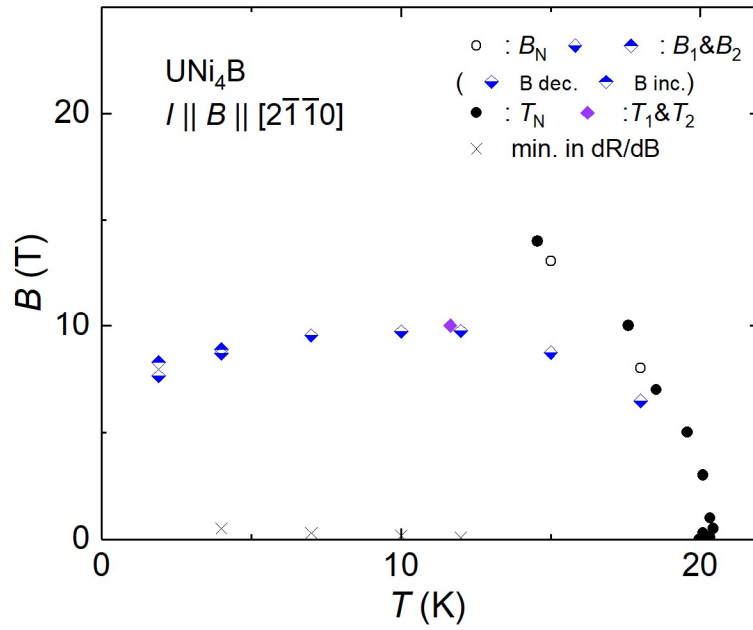


Fig. 5-23 BT phase diagram of UNi₄B obtained by resistivity measurement for $I \parallel B \parallel [2\bar{1}10]$. Black circles indicate T_N and B_N . Blue diamonds may corresponds to B_1 and B_2 observed in magnetization. Upper half filled is obtained from ρ_{inc} . Lower half filled obtained from ρ_{dec} . The symbol “ $\times$ ” indicates inflection point of ρ .

5.6.2 Magnetoresistance for longitudinal magnetic field $B \parallel [0110]$

Figure 5-24 shows T dependence of ρ for $I \parallel B \parallel [0110]$ at $B = 0, 1, 3, 5, 7, 10$, and 14 T. It is almost the same with ρ for $I \parallel [2110]$ at 0 T. The absolute value of ρ is roughly $20 \mu\Omega\text{cm}$ larger than ρ for $I \parallel [2110]$. However, it is difficult to conclude that it is significant because absolute value is easily changed at the estimation of a distance of V - V contacts. When magnetic field is applied, ρ is also suppressed. However, jump anomaly is still significant in the magnetic field of 14 T. It may indicate antiferromagnetic correlation still survives at $B = 14$ T.

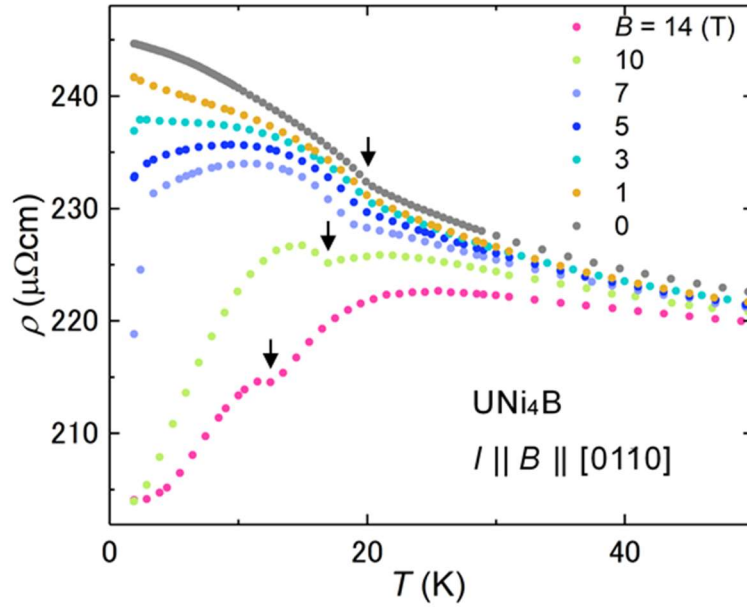


Fig. 5-24 Resistivity ρ vs T for $I \parallel B \parallel [0110]$ at $B = 0, 1, 3, 5, 7, 10$, and 14 T. The measurement was performed only in the condition of FC. Black arrows denote ordering temperatures T_N .

Figure 5-25 shows B dependence of ρ for $T = 1.9, 4, 7, 10, 12, 15, 18,$ and 21 K. The features of ρ is similar to ρ for $I \parallel [2110]$ except for another anomaly B_2 observed around 10 T. The steep step anomaly observed around 8 T is named B_1 in this case. A step at B_1 is enhanced greatly by decreasing temperature while one at B_2 is suppressed and finally flipped around 7 K. The inflection points of ρ in the low B are also put into BT phase diagram shown in Fig. 5-26. By comparing with Fig. 5-12, one can realize that it is not accompanied with low-field anomalies observed in magnetization.

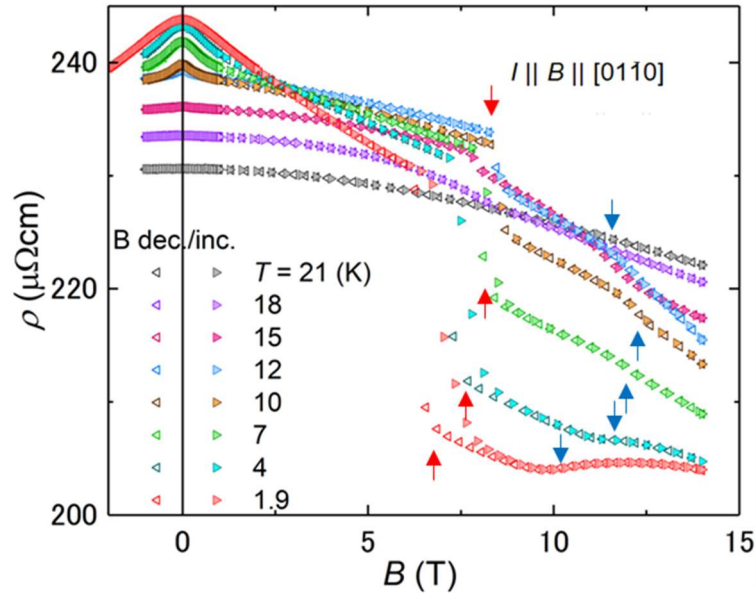


Fig. 5-25 ρ vs B for $I \parallel B \parallel [0110]$ at $T = 1.9, 4, 7, 10, 12, 15, 18,$ and 21 K. The symbols of $\blacktriangleleft$ ($\blacktriangleright$) are ρ_{dec} (ρ_{inc}), respectively. Red and blue arrows indicate anomalies that correspond to the transitions from AF to SR1 (B_1) and from SR1 to SR2 (B_2), respectively.

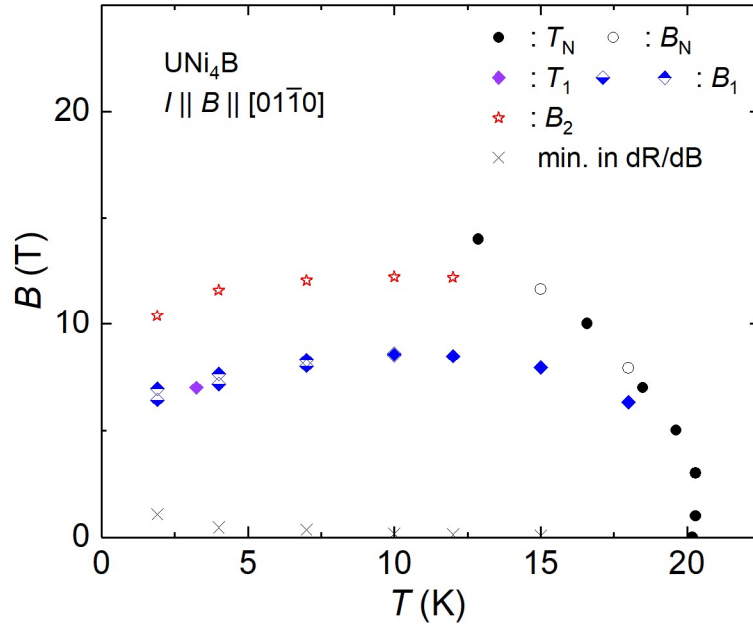


Fig. 5-26 BT phase diagram of UNi₄B obtained by resistivity measurement for $I \parallel B \parallel [01\bar{1}0]$. Black circles are T_N and B_N . Blue diamonds and red stars are B_1 and B_2 . Upper half filled is obtained from ρ_{inc} . Lower half filled obtained from ρ_{dec} . $\times$ are inflection point of ρ .

5.6.3 Magnetoresistance for longitudinal magnetic field $B \parallel [0001]$

Figure 5-27 shows temperature variation of resistivity ρ for $I \parallel B \parallel [0001]$ at $B = 0, 3, 7, 10$, and 14 T. The absolute value of ρ for $I \parallel [0001]$ is twice as small as that for $I \parallel [0110]$ or $[2110]$. There is a kink anomaly at T_N . This is consistent with the previous results. ρ is not affected by magnetic field up to 14 T.

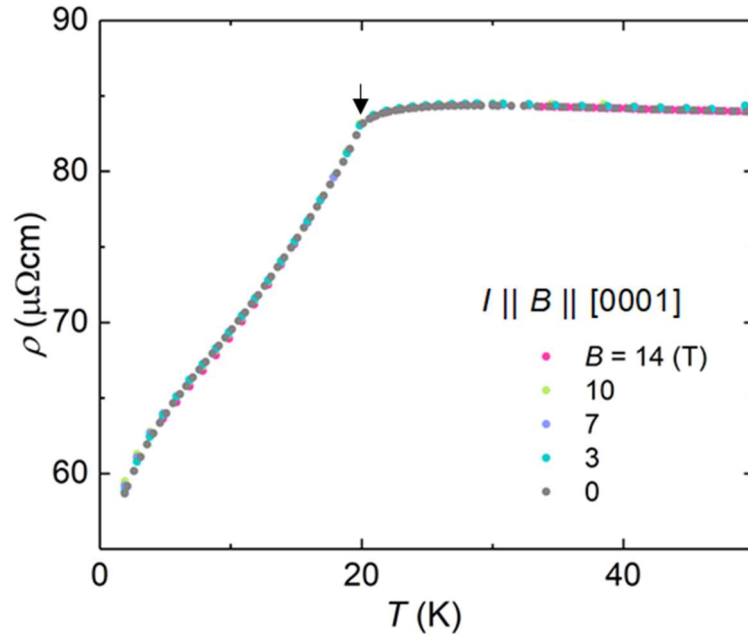


Fig. 5-27 Resistivity ρ vs T for $I \parallel B \parallel [0001]$ at $B = 0, 3, 7, 10$, and 14 T. Black arrow indicates AF ordering temperature T_N .

5.7 Thermal expansion and magnetostriction

Linear thermal expansion is measured by using a miniature capacitance cell. A sample used for magnetization measurement is carefully polished again to obtain perfect parallel plains and used for the measurement. Measurements were performed in the condition of longitudinal magnetic field. Hereafter, I use a notation of $l_{[hklm]}$ and $\alpha_{[hklm]}$ to describe the length and the coefficient of linear thermal expansion of the sample in the direction of $[hklm]$.

Table. 5-5 The summary of measurement conditions. Sample size is $[2110] \times [0110] \times [0001] = 2.23 \times 1.67 \times 1.80 \text{ mm}^3$. B and T are magnetic field and temperature, respectively.

orientation	B (T)	T (K)
$B \parallel [2110], [0110]$	-1 – 14	2.1, 4, 7, 10, 12, 15, 18, 21
$B \parallel [0001]$	-1 – 14	2.2, 4, 7, 10, 15, 21
$l_{[2\bar{1}\bar{1}0]}, l_{[01\bar{1}0]}, l_{[0001]}$	0	0 – 30

5.7.1 Comparison of α with previous results

At first, it should be claimed that the accuracy of this measurement is not so high. Figure 5-28 shows temperature dependence of α for each crystal axes for $B = 0$ T. $\alpha_{[2\bar{1}10]}$ and $\alpha_{[01\bar{1}0]}$ shows a drop at T_N while $\alpha_{[0001]}$ shows a peak. The accuracy of the present data has obviously less than the previous data given by S.A.M Mentink *et al.* [24], while the behavior of α is more less the same. However, fortunately, the condition got better when I performed the field-scan measurement. In addition, since the anomaly emerged at B_1 and B_2 is sufficiently large, we can discuss them.

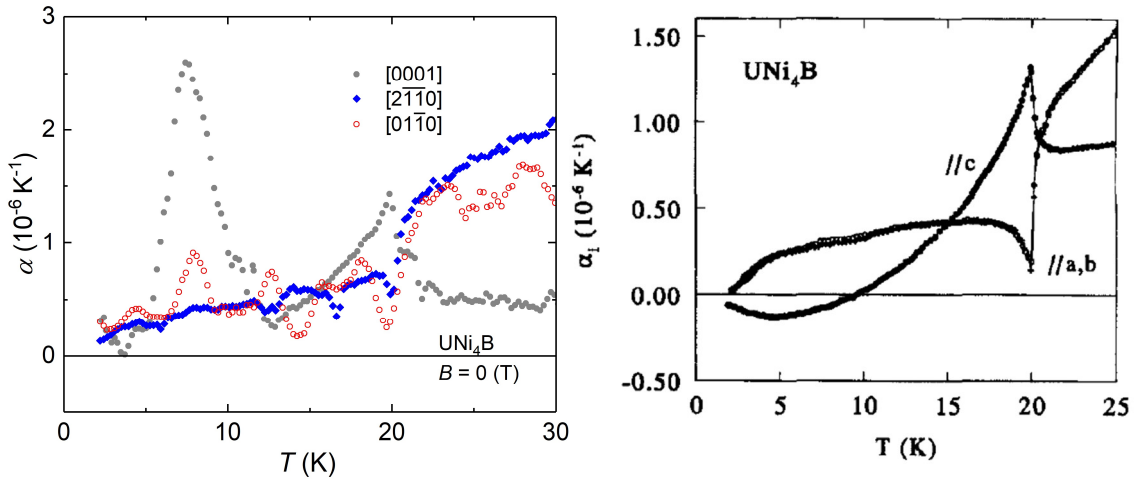


Fig. 5-28 Temperature dependence of the coefficient of linear thermal expansion α in (LHS) the present measurement and (RHS) the previous measurement [24]. a , b , and c in the previous one means each crystal axis of $[2\bar{1}10]$, $[01\bar{1}0]$, and $[0001]$, respectively.

5.7.2 Magnetostriction for $B \parallel [2110]$, $l_{[2110]}$

Magnetic field dependence of the relative change of the sample length $d\ell/\ell$ for $B \parallel [2110]$ at several temperatures are shown in Fig. 5-28. $d\ell/\ell$ tends to get smaller by increasing B . The step like anomaly that could corresponds to B_1 and B_2 observed in magnetization found around 8 T. The large field step of the measurement hinders distinguishing them.

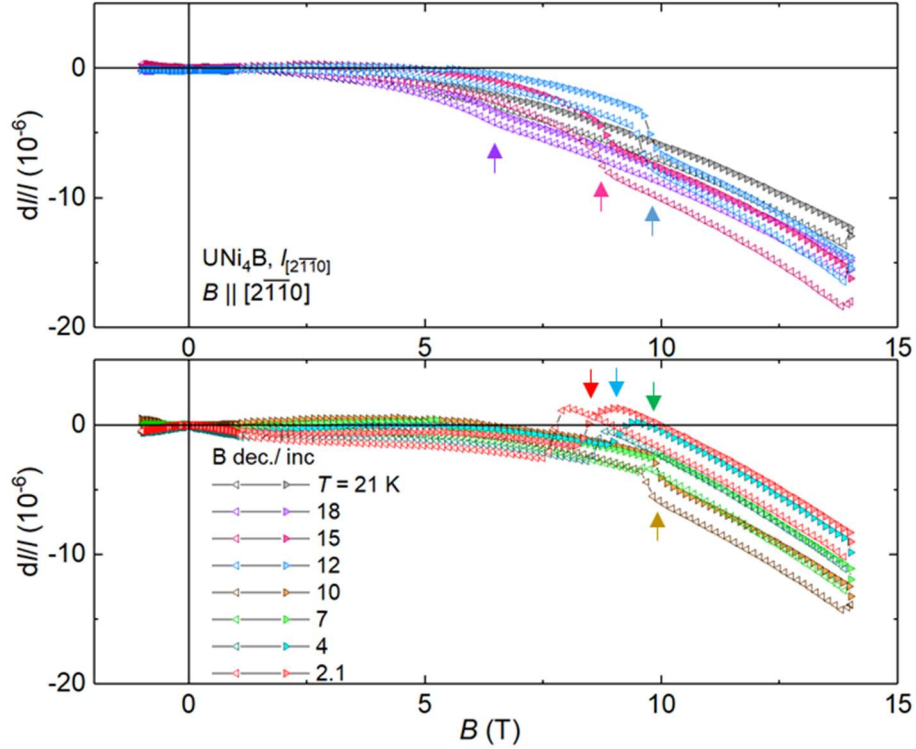


Fig. 5-29 $d\ell_{[2110]}/\ell_{[2110]}$ vs B for $T = 2.1, 4, 7, 10, 12, 15, 18,$ and 21 K. Data are shifted vertically so as to be $d\ell/\ell = 0$ at 0 T. They are separated into two graphs for the visibility. The symbols of $\blacktriangleright$ ($\blacktriangleleft$) are calculated from $\ell_{[2110]}$ measured in the condition of B increasing (B decreasing), respectively. The arrows indicate ordering fields.

The step height is the order of 10^{-6} , which is not large but not negligible, indicating the lattice and magnetic moment are coupled with each other. It is once enhanced as temperature decreases while the ordering field is shifted to higher field. A trend is changed around 10 K. The step height decreases and the ordering field starts shifting to lower field by decreasing temperature below 10 K. The change of behavior shows a good agreement with other physical properties measured in the present work.

The ordering fields are defined as a peak position of the first derivative of dI/I (not shown). They are named $B_1 + B_2$ and summarized in a BT phase diagram shown in Fig. 5-29. The phase line of $B_1 + B_2$ is in the good agreement with one obtained from resistivity.

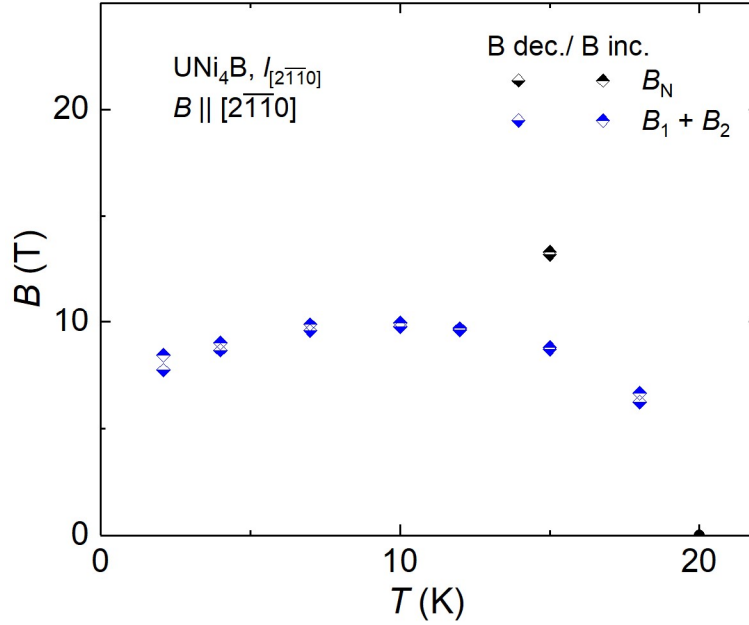


Fig. 5-29 BT phase diagram of UNi₄B obtained from $l_{[2\bar{1}\bar{1}0]}$. The symbols with filled upper (lower) half are obtained from $l_{[2\bar{1}\bar{1}0],\text{inc}}$ ($l_{[2\bar{1}\bar{1}0],\text{dec}}$), respectively.

5.7.3 Magnetostriction for $B \parallel [01\bar{1}0]$, $l_{[01\bar{1}0]}$

Regarding $B \parallel [01\bar{1}0]$, we found two step-like anomalies that seem to be corresponding to B_1 and B_2 . For both steps, the change is negative at first then it is reversed between 12 and 15 K implying a possibility that a competition of specific two correlation corresponds to both transitions. The anomaly at B_2 is larger and blunter than either one at B_1 or ones observed in $l_{[2\bar{1}\bar{1}0]}$.

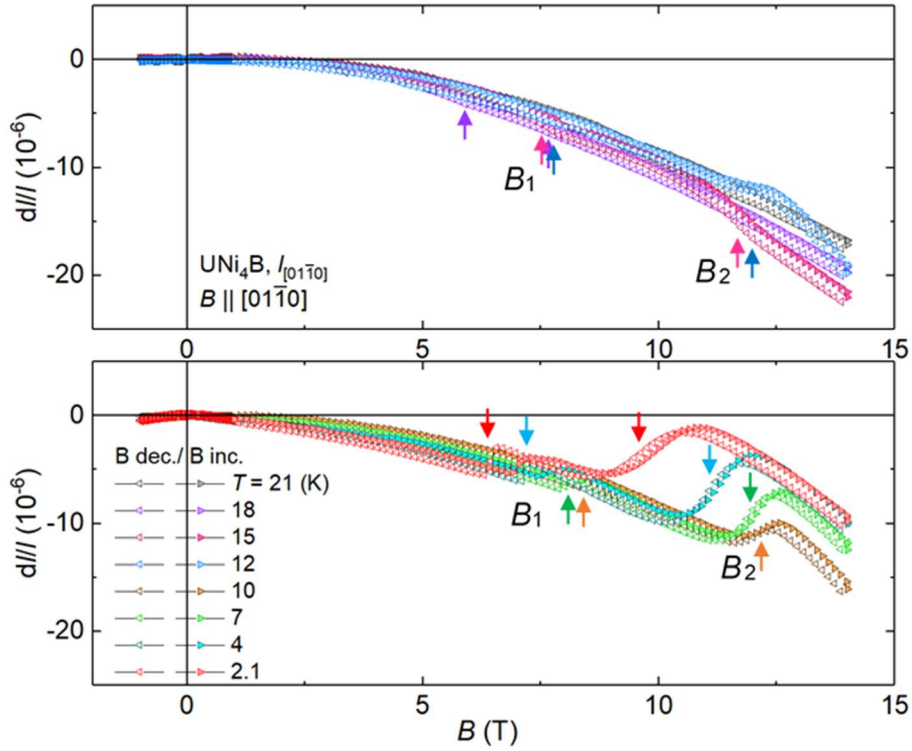


Fig. 5-30 $d l_{[01\bar{1}0]} / l_{[01\bar{1}0]}$ vs B for $T = 2.1, 4, 7, 10, 12, 15, 18$, and 21 K. Data are shifted vertically so as to be $d l / l = 0$ at 0 T. They are separated into two graphs for the visibility. The symbols of $\blacktriangleright$ ($\blacktriangleleft$) are calculated from $l_{[01\bar{1}0]}$ measured in the condition of B increasing (B decreasing), respectively. The arrows indicate ordering fields B_1 and B_2 .

Figure 5-31 shows BT phase diagram of UNi_4B for $B \parallel [01\bar{1}0]$ obtained from $l_{[01\bar{1}0]}$. The obtained diagram is in good agreement with ones obtained from resistivity and magnetization. Two phase boundaries of AF to SR1 and SR1 to SR2 draw parallel phase lines. We found hysteretic behavior at both phase lines. We are not sure whether it is intrinsic or not. It might be better to consider it as a field error of present dilatometry measurement.

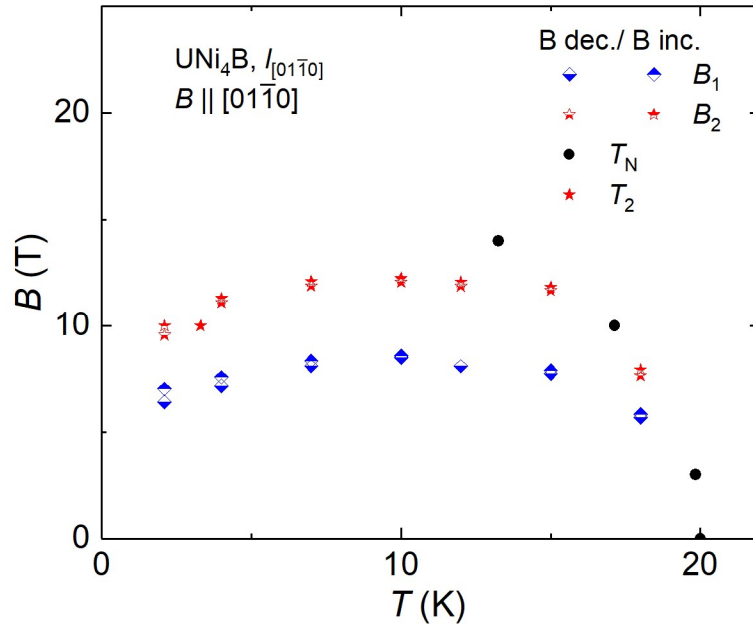


Fig. 5-31 BT phase diagram of UNi_4B obtained from $l_{[01\bar{1}0]}$. The symbols with filled upper (lower) half are obtained from $l_{[01\bar{1}0],\text{inc}}$ ($l_{[01\bar{1}0],\text{dec}}$), respectively. Blue diamonds indicate B_1 , and Red stars indicate B_2 .

5.7.4 Magnetostriction for $B \parallel [0001]$, $l_{[0001]}$

One can find that some data are elevated from zero when data are shifted vertically so as to be $d l/l = 0$. Sometimes, the data sometimes showed a jump when field passes 0 T. However, it was irreproducible. Thus, it is an experimental error. Then, what we can say from these data is that $d l/l$ gradually decreases by increasing magnetic field and any anomaly observed in the accuracy of the measurement.

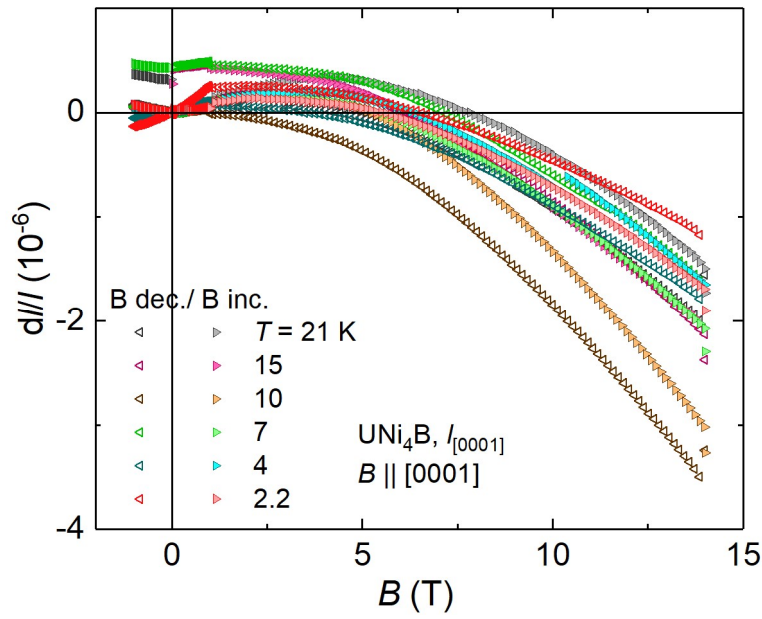


Fig. 5-32 $d l_{[0001]}/l_{[0001]}$ vs B for several temperatures. Data are shifted vertically so as to be $d l/l = 0$ at 0 T. The symbols of $\blacktriangleright$ ($\blacktriangleleft$) are calculated from $l_{[0001]}$ measured in the condition of B increasing (B decreasing), respectively.

5.8 Combined magnetic phase diagram

Finally, we got the combined phase diagram as shown in Fig. 5-33. Phase-boundary lines, which are obscure in magnetization is well identified by other measurements. The existence of the phases of SR1 and SR2 in $B \parallel [01\bar{1}0]$ and SR2 in $B \parallel [21\bar{1}0]$ are confirmed by thermal expansion and resistivity measurements.

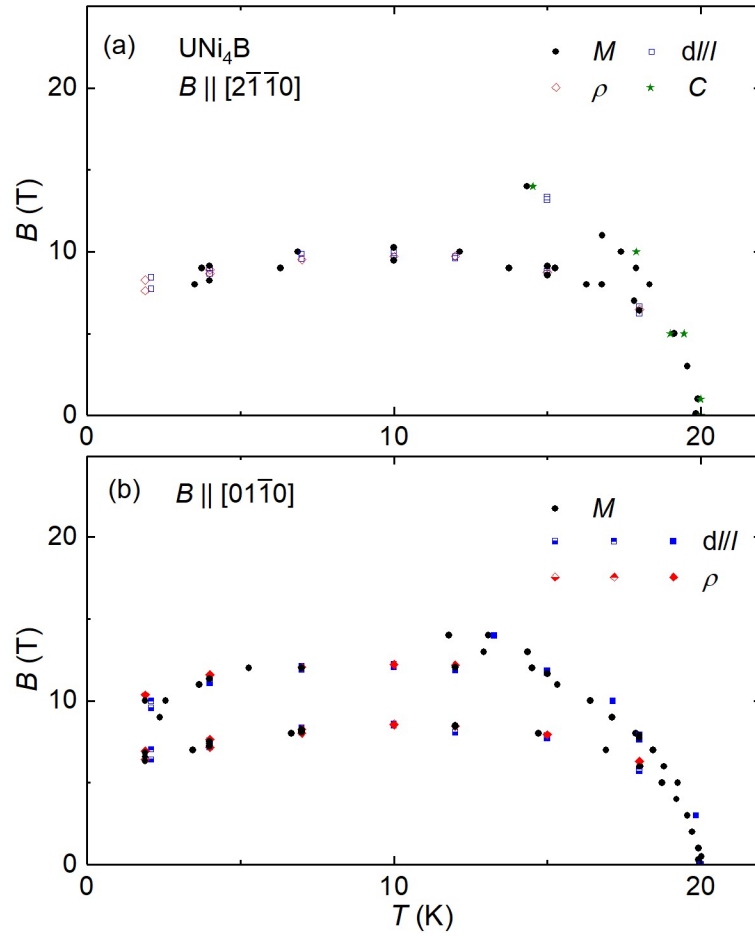


Fig. 5-33 combined BT phase diagram of UNi_4B for (a) $B \parallel [21\bar{1}0]$ and (b) $B \parallel [01\bar{1}0]$. Black circles are obtained from magnetization, Blue squares are from dilatometry, red rhombuses are from resistivity, and green stars are from specific heat.

5.9 Conclusion

Specific heat, magnetization, resistivity, and dilatometry measurements were performed on UNi₄B single crystal synthesized by ourselves as reported in Section 4. We found several remarkable results as follows;

1. SR1 phase is identified in the direction of $B \parallel [2110]$.
2. Metamagnetic like behavior is identified in in-plane magnetic field of less than 0.5 T
3. Crossover of the transitions from AF to SR1 and SR1 to SR2 are identified at ~ 10 K.
4. Hysteretic behavior of magnetization below 5 T is identified in AF phase.

Our experiment revealed that UNi₄B has a complex magnetic phase diagram. The present results imply that the competition of the correlation among magnetic moments and the lattice seems to contribute to such complex behavior, although its mechanics are still not elucidated yet. We would like to note again that ultrasound measurement in our group have revealed recently that Γ_5 electric quadrupole is active in the AF phases of UNi₄B. I suppose that the experimental observation of low-field anomalies and the emergence of SR1 phase for $B \parallel [2110]$ by other experimental techniques could be a first step for further understandings of these behaviors.

6 Concluding remarks

In the present work, I investigated the current-induced magnetization on two antiferromagnetic metallic compounds by means of a commercial SQUID magnetometer to test the validity of the predicted theory regarding toroidal moment and toroidal order in metallic systems. First, I performed magnetization measurements on a candidate of ferroic toroidal ordered metal UNi₄B. Consequently, the following results are obtained;

- a) The applications of electric currents parallel to [2110] and [0001] both induce static magnetization in the direction of [0110] below T_N . $|\Delta M|$ at low temperature is estimated to be $\sim 9.4 \times 10^{-11} \mu_B/U$ per unit current density.
- b) Though this phenomenon should be an intrinsic property, there is a crucial inconsistency that ΔM is induced by the current flow $i \parallel [0001]$, which is an inactive geometry ($i \parallel T$) regarding the ME effects.
- c) the ambiguity of crystal and magnetic structures of this system or the current flowing direction can be regarded as a cause of the inconsistency.

Secondary, I also performed magnetization measurements on a collinear antiferromagnetic compound CeRh_2Si_2 to reveal the necessary and unnecessary conditions required for the ME effects to occur. the obtained results are summarized as follows:

- a) The application of electric currents parallel to $[100]$ induces static magnetization of $\sim 6 \times 10^{-11} \mu_{\text{B}}/\text{Ce}$ per unit current density, in the current direction of $[001]$ only between T_{N1} and T_{N2} .
- b) In the present understanding about the physical properties of CeRh_2Si_2 and the ME effects on metallic systems, the above behavior cannot be explained as the bulk ME effects, and suggests that many antiferromagnets might show the similar ME effects.

These inconsistencies between the theory and the experiments indicate our insufficient understanding on the ME effects and relevant interactions or couplings. Further experimental investigations are necessary to achieve better understanding.

In addition to the above, I improved the growing techniques of single-crystalline samples in the floating zone method. The $\sim 1 \text{ mm/h}$ slow translation without the rotation of the rod is a crucial condition to obtain less mosaic samples. The philosophy of these conditions is to grow single crystals under constant conditions. Since the obtained techniques are quite easy and applicable for many compounds, it would be helpful to the measurements requiring large samples.

Finally, I would like to mention magnetic phase diagram of UNi_4B . The phases of SR1 for $B \parallel [0110]$ and hysteresis in $B < 5 \text{ T}$ and $T < T_{\text{N}}$ are newly found in magnetization on a low-mosaic single crystalline sample grown by means of above procedure. These findings could be helpful for correct description about the ordered phases, the dominant correlations and competitions in UNi_4B , and also the mechanism of ME effect on UNi_4B .

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