Evidence for continuous change of spin states between impurity-induced order and pressure-induced order in $TlCu_{0.985}Mg_{0.015}Cl_3$ probed via muon spin rotation

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Zero- and longitudinal-field muon spin relaxation (ZF- and LF-μSR) measurements were carried out in pressures up to 2 kbar in impurity-doped $TlCu_{0.985}Mg_{0.015}Cl_3$ of which the magnetic phase-transition temperature under ambient pressure in zero field is 2.85 K. The spontaneous muon spin precession, which indicates the existence of a long-range coherent order, is observed above 0.5 kbar at 2.3 K. In ambient pressure, the existence of the static internal magnetic field is confirmed by LF-μSR measurements, however, no rotational signal is observed down to 0.29 K. These results indicate that the crossover reported by IImamura *et al.* [Phys. Rev. B **74**, 064423 (2006)] is the continuous change from a short-range order to a long-range coherent order.

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I. INTRODUCTION

Over the last two decades, curious and unconventional magnetic orderings induced by applying magnetic field, impurity doping, and pressure in spin-gap systems have been reported by many groups,[1–5] and are still attracting much interest in the field of magnetism from the view point of disturbance effects for the spin gap in quantum-spin systems. For the systematic investigation into disturbance effects for gapped quantum-spin systems, there is an advantage if more than one kind of induced magnetic orderings appear in the same gapped system. In $TlCuCl_3$ system, all of those magnetic orderings, which are magnetic field, impurity- and pressure-induced orderings, are reported, and this system is a good candidate for the investigation of relations between those induced ordered states.

$TlCuCl_3$, which is the parent material of the subject compound in this study, has the monoclinic structure (space group $P2_1/c$), and this crystal structure is composed of planar dimers of Cu_2Cl_6.[6] Magnetically, this material is three-dimensionally coupled Cu-3d $S=1/2$ spin dimer system, and the magnetic ground state is spin singlet with excitation gap of $\Delta_{gap}=7.5$ K, which originates from strong intradimer antiferromagnetic interaction.[7] In this system, field-induced magnetic ordering has been investigated extensively and the obtained results are qualitatively well described by the magnon Bose-Einstein condensation theory.[8–10] Pressure-induced magnetic ordering has also been reported in $TlCuCl_3$.[11–13] It is reported that the critical pressure P_c is 0.42 kbar and that the pressure-induced ordered state is an antiferromagnetically ordered state of which the magnetic structure is the same as in the field-induced phase.

In the impurity-doped $Tl(Cu_{1-x}Mg_x)Cl_3$ system, the magnetic phase transition to an ordered state is observed by magnetization and specific-heat measurements and neutron elastic-scattering measurements identified that this impurity-induced ordered state is the antiferromagnetically ordered state of which the magnetic structure is the same with the case of the field-induced phase in $TlCuCl_3$.[14,15] The inelastic neutron-scattering measurement revealed that a finite spin gap still remains below the transition temperature in $Tl(Cu_{1-x}Mg_x)Cl_3$.[16] Recently, Imamura *et al.* reported the pressure-induced magnetically ordered phase by magnetization measurements in $Tl(Cu_{1-x}Mg_x)Cl_3$ with $x=0.012$ and concluded that the change from the impurity-induced phase to the pressure-induced phase is the crossover.[17] However, reports on the crossover from impurity-induced phase to pressure-induced phase mentioned above is based on macroscopic measurements and it is not yet found out the concrete evidence for changes of spin states in the reported crossover by pressure. The purpose of this study is to investigate this crossover by the microscopic probe, the muon spin relaxation technique, and to clarify the microscopic difference between magnetic ground states induced by pressure and by impurity doping.

II. EXPERIMENTS

Single crystals used in this study were grown from a melt by the Bridgman method. The details of crystal growth are given elsewhere.[18] The concentration of x was determined by the inductively coupled plasma-atomic-emission spectrometry method. Muon-spin-relaxation (μSR) measurements were made on $Tl(Cu_{1-x}Mg_x)Cl_3$ with $x=0.015$ at the RIKEN-RAL Muon Facility.[19] Our single-crystal samples were cleaved in helium gas just before the each measurement. Measurements under pressures were carried out using a spin-polarized double-pulsed positive decay-muon beam with an incident muon momentum of 90 MeV/c. Samples were stuffed into the sample space with randomly oriented their crystal axis and are pressurized by ^{4}He gas pressure in a CuBe cell using the newly installed gas-pressurized μSR setup for the RIKEN-RAL Muon Facility.[20] Pressure cell was cooled down to 2.3 K using a usual ^{4}He cryostat. Measurements in ambient pressure were carried out using a spin-polarized single-pulsed positive surface-muon beam with an incident muon momentum of 27 MeV/c. Cleaved crystals were mounted directly on a high-purity silver plate by an

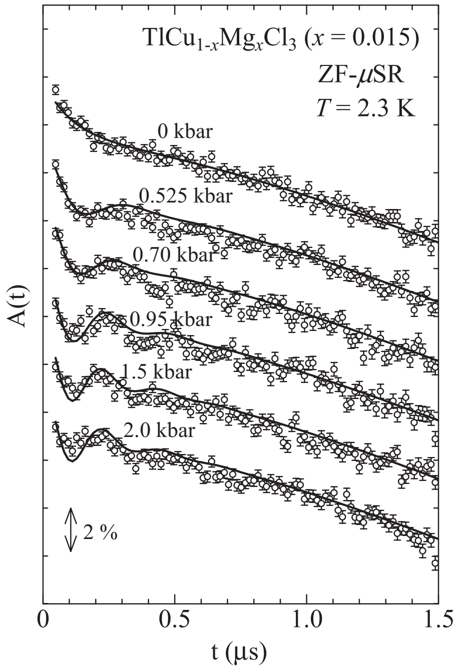

FIG. 1. Time spectra of the ZF-μSR in $TlCu_{1-x}Mg_xCl_3$ with $x=0.015$ under pressures at 2.3 K. Solid lines are fitted results. Each plot is shifted consecutively for clarity.

Apiezon N grease and were covered tightly by a silver film (thickness 50 μm) to ensure thermal contact. Directions of crystal axis were random on the silver plate. In ambient pressure, the sample temperature was controlled with an Oxford ^{3}He cryostat.

In μSR measurements, spin-polarized muons are implanted into samples. Forward and backward counters were located on the upstream and downstream sides of the beam direction, which was parallel to the initial muon spin direction. The asymmetry was defined as

$$A(t) = \frac{F(t) - \alpha B(t)}{F(t) + \alpha B(t)}. \tag{1}$$

Here, $F(t)$ and $B(t)$ were total muon events counted by the forward and backward counters at a time t, respectively. The α is a calibration factor reflecting relative counting efficiencies between the forward and backward counters. The initial asymmetry is defined as $A(0)$. Measured time spectra were analyzed using the WIMDA computer program.[21]

III. RESULTS AND DISCUSSIONS

The magnetic phase transition at ambient pressure is determined by the magnetization measurement to be $T_N = 2.85$ K, which is consistent with the reported phase diagram.[14] Zero-field muon spin relaxation (ZF-μSR) measurements were carried out under pressures up to 2 kbar at 2.3 K. Figure 1 shows ZF-μSR time spectra in various pressures at 2.3 K. Each plot is shifted consecutively for clarity. All spectra are analyzed using the two components function as follows:

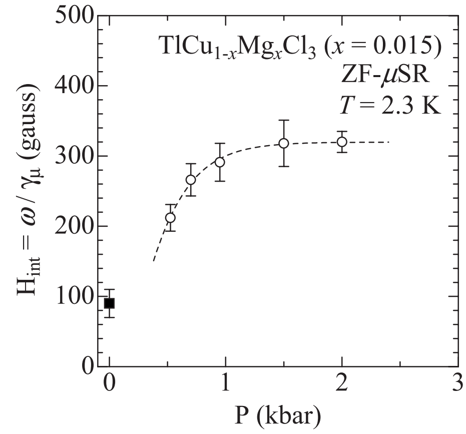

FIG. 2. Pressure dependence of the static internal magnetic field at muon sites deduced from the muon spin rotation frequency at 2.3 K (open circles). Dashed line is guide for the eye. Closed square is the internal magnetic field at muon sites deduced from LF-μSR measurements at 2.3 K as shown in Figs. 5 and 6.

$$A(t) = A_1 e^{-\lambda_1 t} \cos(\omega t + \theta) + A_2 e^{-\lambda_2 t} G_z(\Delta, H_{LF}, t). \tag{2}$$

The first term is the signal from the magnetically ordered region of samples and the second term is that from the large pressure cell and the spin-fluctuating region of samples because it is quite difficult to distinguish the relaxing part $\exp(-\lambda t)$ between the pressure cell and the samples. λ_1 and λ_2 are muon spin relaxation rates, and ω is the rotation frequency. $G_z(\Delta, H_{LF}, t)$ is the static Kubo-Toyabe function, where Δ/γ_μ is the distribution width of nuclear-dipole fields at the muon sites.[22] H_{LF} is the external longitudinal field, so that $H_{LF}=0$ in the case of the zero field. γ_μ is the gyromagnetic ratio of the muon spin ($2\pi \times 13.5534$ kHz/gauss). In this analysis, the double pulse structure is fully taken into account, i.e., the normal relaxation function $f(t)$ becomes $f_{dp}(t)=0.5f(t-t_{sep}/2)+0.5f(t+t_{sep}/2)$,[21] where $t_{sep}=324.5$ ns is the separated time between the double pulses.[19] The conditions in the analysis are as follows: The ratio of the amplitude of the rotational signal and the another part A_1/A_2 is 0.16. Δ/γ_μ and λ_2 are fixed to be 3.8 gauss and 0.081 μs^{-1}, respectively. λ_1 has almost constant value of 8 ± 1 μs^{-1} in the whole range of pressures. In order to grasp the tendency to the development of an order parameter, the main rotational component is considered in the analysis. Fitted results are shown in Fig. 1 as solid lines. Above 0.5 kbar, the spontaneous muon spin precession is observed although no rotational signal is observed in ambient pressure. The spontaneous muon spin precession in zero field indicates that a long-range coherent ordering appears above 0.5 kbar. The static internal magnetic field H_{int} at the muon sites are deduced using the relation of $H_{int}=\omega/\gamma_\mu$. Figure 2 shows the pressure dependence of the static internal magnetic field H_{int} at the muon sites. With increasing pressure, H_{int} increases monotonically and saturates above 1.5 kbar. The pressure dependence of H_{int} corresponds to the change of the ordered moment and suggests the saturation of the development of the ordered moment above $\sim$1 kbar from the view point of

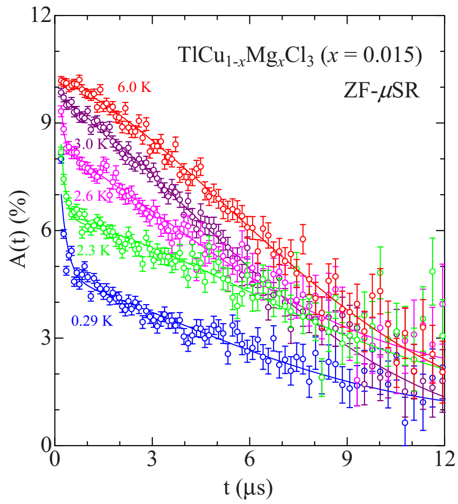

FIG. 3. (Color online) ZF-μSR time spectrum in ambient pressure at 0.29, 2.3, 2.6, 3.0, and 6.0 K. Solid lines are fitted results using the formula (3).

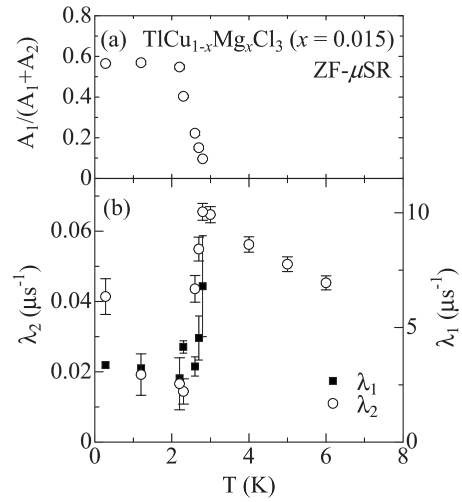

FIG. 4. (a) Temperature dependence of the normalized amplitude A_1. Error bars are within symbols. (b) Temperature dependence of λ_1 (the right side vertical axis, closed squares) and λ_2 (the left side vertical axis, open circles) in the formula (3).

μSR measurements. However, this μSR result in the pressure dependence of H_{int} is not consistent with reported magnetization measurement results for the sample of x=0.012 in pressures, because the step height of the magnetization at the spin-flop transition, which corresponds to the ordered moment, increases with increasing pressure up to 5 kbar.[17] This discrepancy is open problem.

Figure 3 shows the temperature dependence of the ZF-μSR time spectrum in ambient pressure. The constant background from the high-purity silver plate has already been subtracted. Drastic change of the time spectrum is observed and a loss of the initial asymmetry is seen below T_N=2.85 K. All the time spectra in ambient pressure are analyzed using the function

$$A(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} G_z(\Delta, H_{\text{LF}}, t). \quad (3)$$

The first term is the fast relaxation component which appears below T_N and the second term is that of the slow relaxation with the static Kubo-Toyabe function. In the analysis, the initial asymmetries $A(0)$ and Δ/γ_μ are fixed to be 10.3% and 0.98 gauss, respectively. Fitted results are shown in Fig. 3 as solid lines. Temperature dependence of the normalized amplitude A_1 of the fast-relaxation component is plotted in Fig. 4(a). As mentioned below, the origin of the fast relaxation is a static internal magnetic field, thus, the temperature dependence of A_1 relates with the development of the volume fraction of an ordered phase. The volume fraction of a magnetically ordered region of samples is 3/2 of the normalized amplitude A_1 under the assumption that all the fast relaxation component originates from a static internal magnetic field because static internal magnetic fields of which directions are parallel to that of the incident muon beam does not depolarize the muon spins. Thus, the volume fraction of a magnetically ordered region at 0.28 K is roughly estimated to be 85%. A_1 at 2.3 K is large enough to discuss properties of the ground state. Figure 4(b) shows the temperature dependence of muon spin relaxation rates λ_1 and λ_2 in the formula (3). At the transition temperature, the relaxation rate λ_2 has a maximum, and shows a remarkable decrease with decreasing temperature. λ_1 shows a similar temperature dependence below T_N.

In order to determine whether or not the fast relaxation originates from a static internal magnetic field, the longitudinal-field muon spin relaxation (LF-μSR) measurements are carried out in ambient pressure. Time spectra of LF-μSR at 2.3 K are shown in Fig. 5. Solid lines are fitted results using the formula (3). The fast relaxation part in time spectra overlaps, and the long tail of time spectra show parallel shift with increasing H_{LF}. This is the typical behavior in the presence of a static internal magnetic field at the muon sites.[23]

Figure 6 shows the LF dependence of the amplitude A_2 in ambient pressure at 2.3 and 0.29 K obtained from LF-μSR

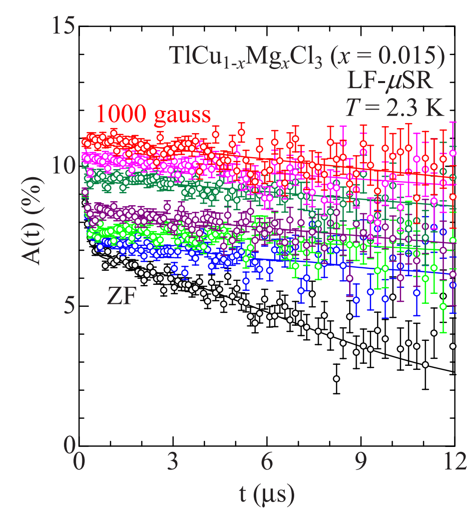

FIG. 5. (Color online) LF-μSR time spectrum under zero pressure in 0, 20, 50, 100, 200, 300, and 1000 gauss. Solid lines are fitted results.

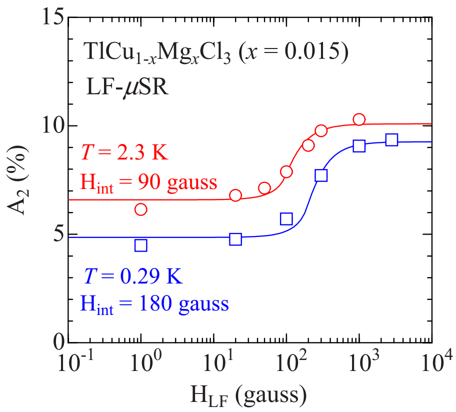

FIG. 6. (Color online) Longitudinal field dependence of the amplitude A_2 of the formula (3) at 2.3 K (open circles) and at 0.29 K (open squares). Error bars are within symbols. Solid lines are fitted results. The deduced static internal magnetic field is 90 ± 20 gauss at 2.3 K and is 180 ± 35 gauss at 0.29 K.

time spectra at each temperature by analyzing using the formula (3). Generally, implanted muon spins precess around the total magnetic field of the internal field and the external field at the muon sites. Thus, the time spectrum changes with increasing the longitudinal field as shown in Fig. 5 and this change is represented by the increase in A_2 in the formula (3). In other word, implanted muon spins are decoupled by longitudinal fields from the static internal magnetic field. The static internal field H_{int} is estimated by the formula

$$A_2(H_{\mathrm{LF}}) - C \propto \frac{3}{4} - \frac{1}{4x^2} + \frac{(x^2-1)^2}{8x^3}\ln\left|\frac{x+1}{x-1}\right|, \qquad (4)$$

where $x = H_{\mathrm{LF}}/H_{\mathrm{int}}$. The constant term C originates from the finite-volume fraction of spin-fluctuating regions. This formula is derived from the assumption that H_{int} has a unique magnitude but random directions to H_{LF}.[24–27] The estimated static internal field H_{int} at the muon sites is 90 ± 20 gauss at 2.3 K and is 180 ± 35 gauss at 0.29 K. The data of 2.3 K is plotted in Fig. 2 (closed square).

As shown in Fig. 3, no rotational signal and a loss of the initial asymmetry are observed in zero field. This result indicates two possibilities in the case of the pulsed muon beam: the first possibility is that there exist a long-range coherent ordered state whose static internal magnetic field at the muon sites is larger than ~600 gauss and the second possibility is the existence of a short-range ordered state whose coherent length is shorter than the resolution limit of the μSR technique and whose internal field is smaller than ~600 gauss. From results of LF-μSR measurements as discussed above, the static internal magnetic field at the muon sites is deduced to be below a few hundred gauss at 0.28 K, thus, the first possibility is ruled out.

In ambient pressure, the magnetic Bragg peaks are observed by elastic neutron-scattering measurements.[15,16] This means that the spin state is coherent in space because the origin of the magnetic Bragg peak is a periodic arrangement of spins. As mentioned above, the spin state is not a long-range coherent ordered state but has the internal static magnetic field of ~90 gauss at 2.3 K and of ~180 gauss at 0.28 K in ambient pressure. Form these results, it is suggested that the system is in a short-range magnetically ordered state in ambient pressure below T_{N}. Thus, we conclude that the crossover reported by Imamura *et al.*[17] is the continuous change from a short-range order to a long-range coherent order without the quantum-critical point during the change.

Here, we speculate about the reason for the continuous change of spin states by pressure. As mentioned above, a finite spin gap still remains below the transition temperature in $Tl(Cu_{1-x}Mg_x)Cl_3$ and this gap would be collapsed by pressure around 0.4 or 0.5 kbar because the critical pressure P_c is 0.42 kbar in the nondoped $TlCuCl_3$. It is suggested that a long-range coherent ordering is impeded by the formation of spin dimers when a finite spin gap remains, and that above a critical pressure P_c, the coherent order develops drastically. It is plausible to consider the model as follows: doped Mg-ions destroy spin dimers locally and unpaired spins are induced. These spins interact one another through the interdimer exchange interaction with excited states of spin dimers and the spin system tends to the magnetic phase transition. In ambient pressure, however, the spin system is divided into islands of a short-range ordered state around Mg ions and the gapped spin-singlet state. Above the critical pressure, the spin gap is collapsed, and islands spread throughout the sample, i.e., a long-range coherent order appears.

In the last, the possibility of another *crossover* is pointed out. In the case of the lightly doping of $x=0.0047$, the appearance of an internal static field is not observed down to 20 mK by μSR measurements although a magnetic phase transition is observed at 0.70 K by the specific-heat measurement.[28] In this study for $x=0.015$, the existence of the internal static field is confirmed but the volume fraction of the static-field region is not 100%. These results suggest a continuous change from the spin-fluctuating state to the short-range ordered state in ambient pressure with increasing the Mg doping. The detail investigation of the Mg concentration dependence of the ground state is on progress.

IV. SUMMARY

In summary, zero- and longitudinal-field muon spin relaxation (ZF- and LF-μSR) measurements were carried out in pressures up to 2 kbar in impurity-doped $TlCu_{1-x}Mg_xCl_3$ with $x=0.015$. The spontaneous muon spin precession, which indicates the existence of a long-range coherent order, was observed above 0.5 kbar at 2.3 K, although no rotational signal was observed in ambient pressure. LF-μSR measurements in ambient pressure revealed the existence of an internal static magnetic field of 90 ± 20 gauss at 2.3 K. These results indicate that the reported crossover by pressure is the continuous change from a short-range order to a long-range coherent order without the quantum-critical point during the change.

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[1] J. C. Bonner, S. A. Friedberg, H. Kobayashi, D. L. Meier, and H. W. J. Blöte, Phys. Rev. B **27**, 248 (1983).
[2] Z. Honda, K. Katsumata, H. Aruga Katori, K. Yamada, T. Oishi, T. Manabe, and M. Yamashita, J. Phys.: Condens. Matter **9**, L83 (1997); J. Phys.: Condens. Matter **9**, 3487(E) (1997).
[3] M. Hase, I. Terasaki, Y. Sasago, K. Uchinokura, and H. Obara, Phys. Rev. Lett. **71**, 4059 (1993).
[4] T. Masuda, K. Uchinokura, T. Hayashi, and N. Miura, Phys. Rev. B **66**, 174416 (2002).
[5] I. Kézsmárki, Sz. Csonka, H. Berger, L. Forró, P. Fazekas, and G. Mihály, Phys. Rev. B **63**, 081106(R) (2001).
[6] W. Shiramura, K. Takatsu, H. Tanaka, K. Kamishima, M. Takahashi, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **66**, 1900 (1997).
[7] N. Cavadini, W. Henggeler, A. Furrer, H.-U. Güdel, K. Krämer, and H. Mutka, Eur. Phys. J. B **7**, 519 (1999).
[8] A. Oosawa, M. Ishii, and H. Tanaka, J. Phys.: Condens. Matter **11**, 265 (1999).
[9] T. Nikuni, M. Oshikawa, A. Oosawa, and H. Tanaka, Phys. Rev. Lett. **84**, 5868 (2000).
[10] F. Yamada, T. Ono, H. Tanaka, G. Misquich, M. Oshikawa, and T. Sakakibara, J. Phys. Soc. Jpn. **77**, 013701 (2008).
[11] K. Goto, M. Fujisawa, T. Ono, H. Tanaka, and Y. Uwatoko, J. Phys. Soc. Jpn. **73**, 3254 (2004).
[12] H. Tanaka, K. Goto, M. Fujisawa, T. Ono, and Y. Uwatoko, Physica B **329-333**, 697 (2003).
[13] Ch. Rüegg, B. Normand, M. Matsumoto, A. Furrer, D. F. McMorrow, K. W. Krämer, H.-U. Güdel, S. N. Gvasaliya, H. Mutka, and M. Boehm, Phys. Rev. Lett. **100**, 205701 (2008).
[14] A. Oosawa, T. Ono, and H. Tanaka, Phys. Rev. B **66**, 020405(R) (2002).
[15] M. Fujisawa, T. Ono, H. Fujiwara, H. Tanaka, V. Sikolenko, M. Meissner, P. Smeibidl, S. Gerischer, and H. A. Graf, J. Phys. Soc. Jpn. **75**, 033702 (2006).
[16] A. Oosawa, M. Fujisawa, K. Kakurai, and H. Tanaka, Phys. Rev. B **67**, 184424 (2003).
[17] H. Imamura, T. Ono, K. Goto, and H. Tanaka, Phys. Rev. B **74**, 064423 (2006).
[18] A. Oosawa and H. Tanaka, Phys. Rev. B **65**, 184437 (2002).
[19] T. Matsuzaki, K. Ishida, K. Nagamine, I. Watanabe, G. H. Eaton, and W. G. Williams, Nucl. Instrum. Methods Phys. Res. A **465**, 365 (2001).
[20] I. Watanabe, Y. Ishii, T. Kawamata, T. Suzuki, F. L. Pratt, R. Done, M. Chowdhury, C. Goodway, J. Dreyer, C. Smith, and M. Southern, Physica B **404**, 993 (2009).
[21] F. L. Pratt, Physica B **289-290**, 710 (2000).
[22] R. Kubo and T. Toyabe, in *Magnetic Resonance and Relaxation*, edited by R. Blinc (North-Holland, Amsterdam, 1967), p. 810.
[23] Y. J. Uemura, T. Yamazaki, D. R. Harshman, M. Senba, and E. J. Ansaldo, Phys. Rev. B **31**, 546 (1985).
[24] N. Nishida (private communication).
[25] I. Watanabe, M. Akoshima, Y. Koike, S. Ohira, and K. Nagamine, Phys. Rev. B **62**, 14524 (2000).
[26] K. Hachitani, H. Fukazawa, Y. Kohori, I. Watanabe, C. Sekine, and I. Shirotani, Phys. Rev. B **73**, 052408 (2006).
[27] F. L. Pratt, J. Phys.: Condens. Matter **19**, 456207 (2007).
[28] T. Suzuki, F. Yamada, I. Watanabe, T. Matsuzaki, T. Goto, A. Oosawa, and H. Tanaka, J. Phys. Soc. Jpn. **78**, 074705 (2009).