^{11}B NMR Study of $Ce_xLa_{1-x}B_6$

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We have carried out ^{11}B NMR experiments on single crystals of $Ce_xLa_{1-x}B_6$ in order to investigate the nature of phase IV. The NMR spectrum undergoes an appreciable broadening by the internal magnetic field as T is lowered in phase IV, and the nuclear spin-lattice relaxation rate, $1/T_1$, exhibits a sharp peak around the phase I-IV boundary. Also, in phase III the amplitude of the antiferromagnetic (AFM) moment is large enough even just below the phase IV-III transition, which suggests that the AFM moment grows considerably in phase IV. These results support the view that phase IV is an AFM ordered phase.

Key words: ^{11}B NMR; $Ce_xLa_{1-x}B_6$; Phase IV; Nuclear Spin-lattice Relaxation; Antiferromagnetic Transition.

1. Introduction

CeB_6 has an interesting phase diagram, which consists of the paramagnetic phase I above T_Q = 3.3 K, the antiferroquadrupolar (AFQ) phase II between T_Q and T_N = 2.3 K, and the antiferromagnetic (AFM) phase III below T_N in H = 0. There was a serious contradiction in the interpretation of phase II between the neutron scattering [1 - 3] and NMR experiments [4 - 6]. Recently it was pointed out that this discrepancy can be resolved by considering the hyperfine coupling between the octupolar moment of the Ce ion and the ^{11}B nuclear spin [7 - 9]. Furthermore, quite recently it has been now established that the octupolar moment plays an important role not only in phase II but also in phase III [10]. Thus, the octupolar momemt plays a key role to understand the phase diagram of CeB_6.

The recently discovered new phase, callled phase IV, for $x \leq 0.8$ in $Ce_xLa_{1-x}B_6$ has also attracted attention. For x = 0.75, phase IV appears between phase I and III. It exists only in a narrow region of the H-T plain. At H = 0, phase IV exists between 1.3 and 1.7 K, and it exists up to 6 kOe [11]. Phase IV is considered to be an AFM state due to a huge discontinuous decrease in the elastic constant [12], the presence of a sharp peak in the specific heat [13], and a cusp in the magnetic susceptibility measurements [14] at the phase I-IV boundary. However, no magnetic superlattice peak has been discovered yet by a neutron scattering experiment [15]. The order parameter of phase IV is still unknown. Further studies are necessary to clarify the nature and get more information about phase IV. In order to get a final conclusion for the order parameter in phase IV, an experiment on a microscopic probe is required. The nuclear magnetic resonance (NMR) technique is a powerful method to obtain microscopic information of the magnetic state.

In this paper, we present extensive NMR studies on single crystals of $Ce_xLa_{1-x}B_6$ (x = 1, 0.75) in order to elucidate the nature of phase IV.

2. Experimental

Single crystalline samples were grown by the traveling-solvent floating-zone method [16]. The sample was shaped to a sphere with 5 mm diameter in order to avoid the correction for the demagnetizing field, which is expected to be compensated by the Lorentz field. The NMR measurements were carried out at temperatures below 4.2 K by a conventional

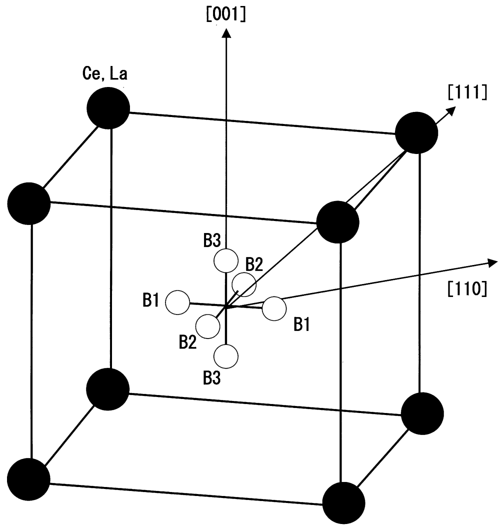

Fig. 1. Crystal structure of $Ce_xLa_{1-x}B_6$.

phase-coherent pulsed spectrometer. A field-swept ^{11}B NMR spectrum was obtained by plotting the spin-echo amplitude as a function of the magnetic field. The nuclear spin-lattice relaxation time, T_1, was measured by the saturation recovery method.

$Ce_xLa_{1-x}B_6$ has a cubic CaB_6-type structure with Ce (La) ions at the corners and boron octahedra at the center, as shown in Figure 1. The principal axis of the electric field gradient (EFG) tensor at B site is found to be parallel to the four-fold axis at each position of the cubic lattice. The external field being rotated in the $(1\bar{1}0)$-plane, there exist two kinds of B sites, (B1, B2) and B3. This notation is shown in Figure 1. The principal axes of these two groups make different angles with the external magnetic field.

3. Results and Discussion

Figures 2(a), (b), and (c) show nine temperatures the NMR spectra of $Ce_{0.75}La_{0.25}B_6$ observed at 6.5 MHz under magnetic fields along the [001]-,

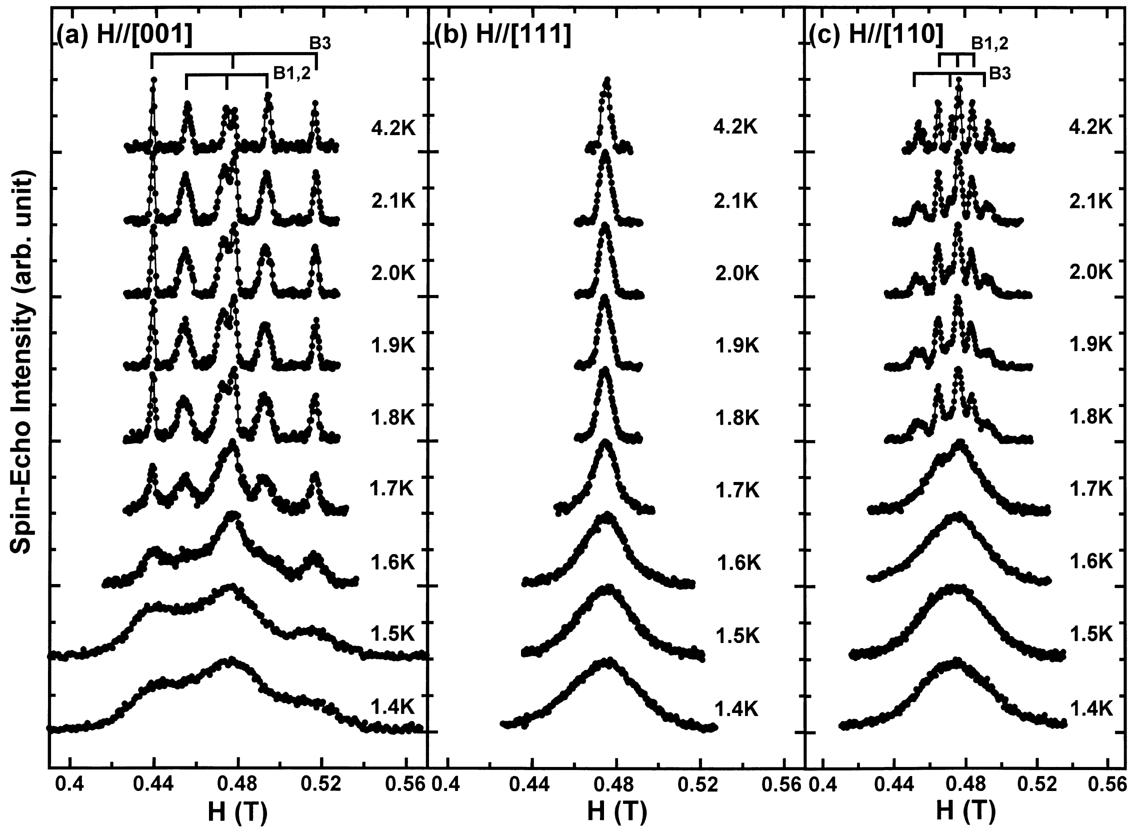

Fig. 2. T dependences of the NMR spectra of $Ce_{0.75}La_{0.25}B_6$ at 6.5 MHz for (a) $H \parallel [001]$, (b) $H \parallel [111]$, and (c) $H \parallel [110]$.

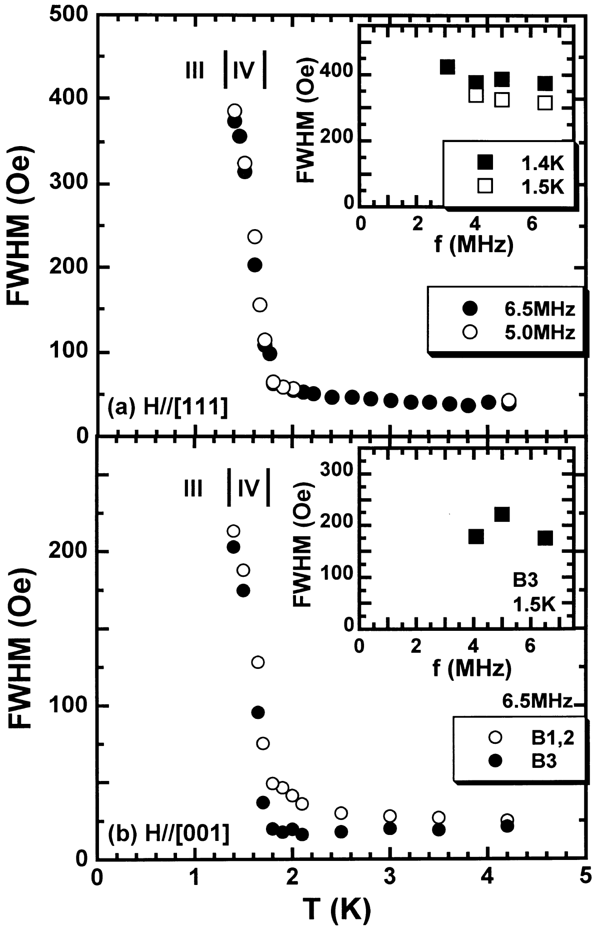

Fig. 3. T dependences of the full-width at the half-maximum (FWHM) of the spectra of $Ce_{0.75}La_{0.25}B_6$ for (a) H ||[001] and (b) H ||[111]. Insets show H dependences of FWHM.

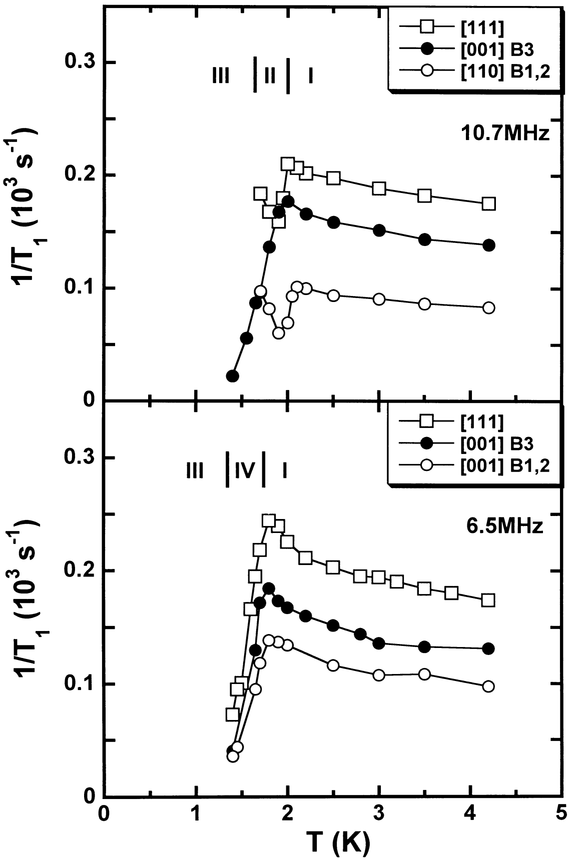

Fig. 4. T dependences of the nuclear spin-lattice relaxation rates, $1/T_1$, of $Ce_{0.75}La_{0.25}B_6$ at the frequencies of (a) 10.7 MHz and (b) 6.5 MHz. Solid lines are guides to eye.

[111]-, and [110]-axes, respectively. In the paramagnetic phase I above 1.7 K, the spectra for H ||[001] and H ||[110] consist of two sets of three lines due to the electric quadrupole interaction, because I=3/2 for the ^{11}B nucleus. The splitting of the central transition line, which is the same as CeB_6 [4], arises from the ferromagnetic moments induced at the Ce sites. For H ||[111], however, the first order contribution of the quadrupole interaction disappears for all boron sites, and the spectrum consists of only one resonance line. The spectrum is composed of sharp lines, and we can estimate the nuclear quadrupole frequency as 0.53 MHz from the splitting of the satellite lines, in good agreement with the results on CeB_6 [4] and LaB_6 [17].

Figures 3(a) and (b) show the temperature dependences of the full-width at half-maximum(FWHM) of the spectra under the magnetic field along the [111]- and [001]-axis, respectively. In phase I, the T dependence of the FWHM is small. On the other hand, in phase IV the spectrum undergoes an appreciable broadening symmetrically for all B sites as T is lowered below 1.7 K, which is independent of the direction of the external magnetic field. The local magnetic field at the B sites can be detected from the splitting and/or broadening of the NMR spectrum, and this broadening of the spectrum means that there is an internal magnetic field at each B site in phase IV, suggesting that phase IV is an AFM one. If phase IV is a simple AFM state, the internal magnetic field is expected to be cancelled at some B sites, because the B nuclei are located at highly symmetrical sites for the surrounding Ce ions. The structure of the spectrum of

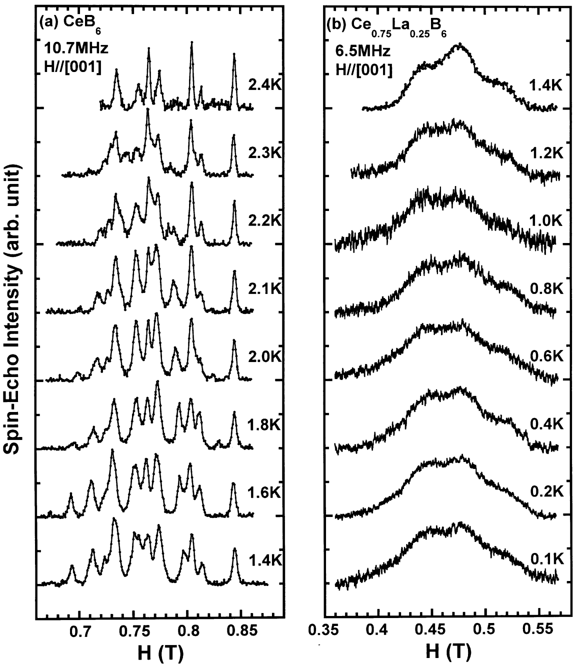

Fig. 5. The NMR spectra at eight temperatures for H ||[001] in phase III of (a) CeB_6 and (b) $Ce_{0.75}La_{0.25}B_6$.

phase IV is almost the same as that of phase I, except for the broadening of FWHM, in contrast to phase III with a complicated spin structure, where many resonance peaks appear. Thus, the magnetic structure of phase IV is not expected to be complicated, and is suggested to be incommensurate. The insets show the magnetic field dependences of FWHM. FWHM is almost independent of the external magnetic field, in contrast to the case of phase II, which is an AFQ ordering state accompanied with a field-induced antiferro-octupolar ordering.

Figures 4(a) and (b) show the T dependences of the nuclear spin-lattice relaxation rates, $1/T_1$, measured at the frequencies of 10.7 and 6.5 MHz, respectively. For the magnetic fields along the [001]- and [110]-axes, the measurements were made on the satellite lines to ensure that only signal from a single site was detected. Such measurements are more reliable than those made on the central transition in which lines from both sites overlap. As seen in the figure, in case of 10.7 MHz, $1/T_1$ exhibits sharp peaks around both the phase I-II and II-III transition point, except for H ||[001]. On the other hand, in case of 6.5 MHz $1/T_1$ exhibits a sharp peak only around 1.7 K, close to the phase I-IV transition point. This is thought to originate from critical magnetic fluctuations towards a magnetic phase transition. In contrast to the phase I-IV boundary, there is no sign of a remarkable anomaly around the phase IV-III boundary for all directions, where the anomaly in the specific heat measurements is small, too [13] This suggests that the magnetic property of phase IV is similar to that of the AFM phase III, and that phase IV is an AFM phase. Thus it is very important to investigate the physical properties of phase III. But, it is difficult to measure $1/T_1$ in phase III because the many signals overlap, as shown below.

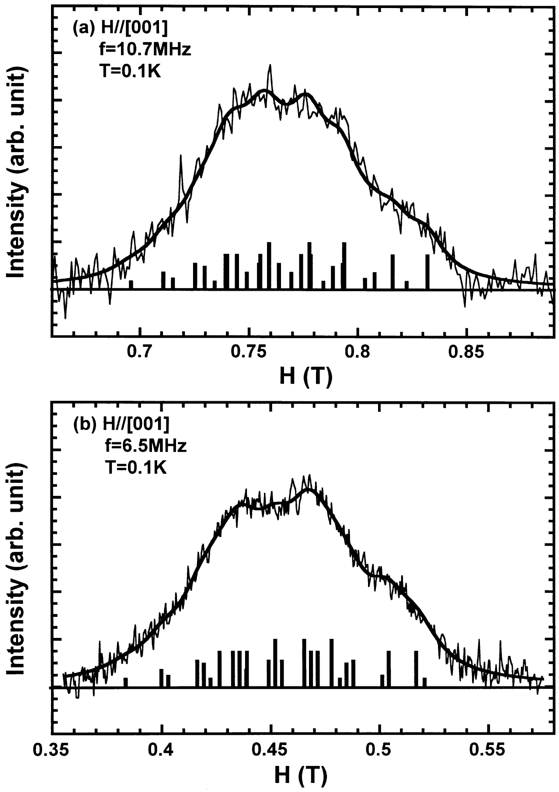

Fig. 6. The NMR spectra of $Ce_{0.75}La_{0.25}B_6$ at 0.1 K in phase III for H || [001] at (a) 10.7 MHz and (b) 6.5 MHz.

Next, we present the spectra in the AFM phase III. Figures 5(a) and (b) show at eight low temperatures the NMR spectra for H || [001] of CeB_6 and $Ce_{0.75}La_{0.25}B_6$, respectively. In CeB_6 the spectrum is composed of sharp peaks. Below 2.3 K, many lines emerge in the lower magnetic field region accompanying the occurrence of the static internal field by the spin ordering. In $Ce_{0.75}La_{0.25}B_6$ the spectrum is considerably broadened by the La doping, but the spread

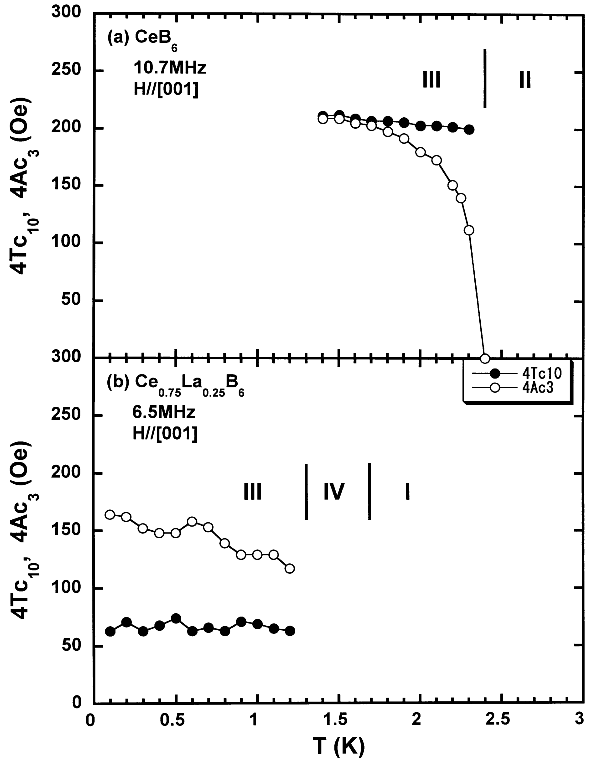

Fig. 7. T dependences of $4Tc_{10}$ and $4Ac_3$ of (a) CeB_6 and (b) $Ce_{0.75}La_{0.25}B_6$ for H ||[001].

of the spectrum towrds the lower field region is similar to the case of CeB_6.

Next, we estimate the spectrum by the Sakai model [10], which reproduces the spectrum in phase III of CeB_6. Figures 6(a) and (b) show the ^{11}B NMR spectra of $Ce_{0.75}La_{0.25}B_6$ at 0.1 K in phase III for H ||[001] at the frequencies of 10.7 and 6.5 MHz, respectively. According to the model, there are 9 non-equivalent B sites with satellite lines (27 peaks) in this case. The solid lines in the Fig. 6 shows a fit to the experiment. The resonance lines obtained are shown by vertical bars at the bottom in Figs. 6 (a) and (b). The lines that are situated closely compose a broad peak. The assumed parameters, defined in [10], are $4M(c_9 - c_1)$ = 265 Oe, $4Ac_3$ = 147 Oe, and D = $4Tc_{10}$ = 80 Oe, with the Lorentzian width 206 Oe for 10.7 MHz, and $4M(c_9-c_1)$ = 196 Oe, $4Ac_3$ = 164 Oe, and D = $4Tc_{10}$ = 63 Oe, with the Lorentzian width 230 Oe for 6.5 MHz, Here, A is the amplitude of the AFM moment, T is the amplitude of the octupolar moment T_{xyz}, M is the uniform magnetization along the [001]-axis, and the c_i's are coupling constants. As seen in Fig. 6, the spectrum is well reproduced by this model. This suggests that phase III of $Ce_{0.75}La_{0.25}B_6$ is similar to that of CeB_6. Also, it is known that the amplitude of the octupolar moment decreases by La-doping, in comparison with the case of CeB_6.

Figures 7(a) and (b) show the T dependences of the parameters $4Tc_{10}$ and $4Ac_3$, related to the amplitude of the octupolar and the AFM moments in phase III of CeB_6 and $Ce_{0.75}La_{0.25}B_6$, respectively. In case of CeB_6, $4Tc_{10}$ has a weak T dependence, which characterizes in the field-induced antiferromagnetic octupolar ordering of phase II, and grows up sufficiently in phase II. Also, $4Ac_3$ grows up suddenly below the phase II-III boundary, because of the order parameter in the AFM phase III. On the other hand, in case of $Ce_{0.75}La_{0.25}B_6$, $4Tc_{10}$ is almost T independent. Also, $4Ac_3$ has a weak T dependence and is large enough just below the phase IV-III boundary, in contrast to the phase II-III boundary. These results indicate that the AFM moment may grow up well in phase IV, suggesting that phase IV is an AFM phase.

4. Summary

In summary, the ^{11}B NMR experiments were carried out on single crystalline samples of $Ce_xLa_{1-x}B_6$ in order to elucidate the nature of phase IV. In $Ce_{0.75}La_{0.25}B_6$, the NMR spectrum undergoes an appreciable broadening as T is lowered in phase IV. Also, $1/T_1$ exhibits a sharp peak around the phase I-IV boundary, originating from critical magnetic fluctuations towards a magnetic phase transition. In contrast to the phase I-IV boundary, there is no sign of a remarkable anomaly around the phase IV-III boundary, which is consistent with the results of the specific heat measurements. It suggests that the magnetic property of phase IV is similar to that of the AFM phase III. Also, from the analyses of the spectra in phase III, the amplitude of the AFM moment is large enough even just below the phase IV-III transition point, which suggests that the AFM moment may grow well in phase IV. Thus, the NMR studies have assured that phase IV can be considered to be a kind of AFM ordered phase. As for the nature of phase IV, two possibilities are discussed. One is the AF octupolar ordering [18 - 20], and the other is the incommensurate AF magnetic ordering [21]. In case of the AF octupolar ordering, two-fold degeneracies of the spin degrees of the freedom are expected to remain, but this is inconsistent with the results of specific heat measurements, which suggest that the four-fold degeneracies in the quartet ground state are lifted into four discrete levels in phase IV [13]. On the other hand, the results of the specific heat measurements are consistent with the incommensurate AF magnetic ordering, which is strongly supported by the similarity between the physical properties of $Ce_{0.75}La_{0.25}B_6$ and PrB_6 [21], which shows the successive phase transition to the incommensurate AF magnetic ordered state at 7 K and the commensurate AF magnetic ordered state at 4.2 K. From these results, phase IV is considered to be an incommensurate AF magnetic ordering phase, and the phase IV-III transition is presumed to be a spin re-orientation transition from an incommensurate to a commensurate phase. In general, an incommensurate-commensurate transition occurs as a first order one. In fact, a hysteresis is observed in the magnetization measurements around the phase IV-III transition [14]. However, these results are inconsistent with those obtained by recent neutron scattering and μSR experiments. It is not easy to distinguish the AFM ordering and the octupolar ordering and to elucidate the nature of phase IV on the basis of the present data alone. Detailed magnetic investigation is necessary to get a final conclusion.

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[1] J. M. Effantin, P. Burlet, J. Rossat-Mignod, S. Kunii, and T. Kasuya, Valence Instabilities, ed. P. Wachter and H. Boppart, North-Holland Publishing Company, 1982, p. 559.
[2] J. M. Effantin, J. Rossat-Mignod, P. Burlet, H. Bartholin, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **47**&**48**, 145 (1985).
[3] W. A. C. Erkelens, L. P. Regnault, P. Burlet, J. Rossat-Mignod, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **63**&**64**, 61 (1987).
[4] M. Kawakami, S. Kunii, K. Mizuno, M. Sugita, T. Kasuya, and K. Kume, J. Phys. Soc. Japan **50**, 432 (1981).
[5] M. Kawakami, K. Mizuno, S. Kunii, T. Kasuya, H. Enoki, and K. Kume, J. Magn. Magn. Matter. **30**, 201 (1982).
[6] M. Takigawa, H. Yasuoka, T. Tanaka, and Y. Ishizawa, J. Phys. Soc. Japan **52**, 728 (1983).
[7] O. Sakai, R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Japan **66**, 3005 (1997).
[8] R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Japan **66**, 1741 (1997).
[9] R. Shiina, O. Sakai, H. Shiba, and P. Thalmeier, J. Phys. Soc. Japan **67**, 941 (1998).
[10] O. Sakai, R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Japan **68**, 1364 (1999).
[11] M. Hiroi, M. Sera, N. Kobayashi, and S. Kunii, Phys. Rev. B **55**, 8339 (1997).
[12] S. Nakamura, T. Goto, and S. Kunii, J. Phys. Soc. Japan **64**, 3941 (1995).
[13] O. Suzuki, T. Goto, S. Nakamura, T. Matsumura, and S. Kunii, J. Phys. Soc. Japan **67**, 4243 (1998).
[14] T. Tayama, T. Sakakibara, K. Tenya, H. Amitsuka, and S. Kunii, J. Phys. Soc. Japan **66**, 2268 (1997).
[15] M. Kohgi et al., unpublished.
[16] S. Kunii, J. Phys. Soc. Japan **57**, 361 (1988).
[17] J.L. Gavilano, Sh. Mushkolaj, D. Rau, H. R. Ott, A. Bianchi, D. P. Young, and Z. Fisk, Phys. Rev. B **63**, 140410(R) (2001).
[18] Y. Kuramoto and H. Kusunose, J. Phys. Soc. Japan **69**, 671 (2000).
[19] H. Kusunose and Y. Kuramoto, J. Phys. Soc. Japan **70**, 1751 (2001).
[20] T. Takikawa, T. Sakakibara, K. Matsuhira, K. Tanya, H. Amitsuka, and S. Kunii, Physica **B 281** & **282**, 561 (2000).
[21] S. Kobayashi, M. Sera, M. Hiroi, N. Kobayashi, and S. Kunii, J. Phys. Soc. Japan **69**, 926 (2000).