Evolution from Magnetism to Unconventional Superconductivity in a Series of $Ce_xCu_2Si_2$ Compounds Probed by Cu NQR

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We report on the basis of Cu-NQR measurements that the ground state in a series of $Ce_xCu_2Si_2$ compounds evolves from a magnetically ordered phase at $x = 0.975$ to a heavy-electron superconducting (SC) phase at $x = 1.025$. We have found that the sample of $x = 0.99$ does not exhibit any trace of magnetic phase transition down to 0.012 K. Slow magnetic fluctuations with low frequencies comparable to the NQR frequency develop rapidly below $T_m \sim 1.2$ K. This unusual "critical magnetic phase" can coexist with the SC phase. For the samples of $x = 1.00$ and 1.025 such a state is expelled by the onset of the SC state. [S0031-9007(99)09429-6]

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Since the discovery of heavy-fermion superconductivity (HFS) in $CeCu_2Si_2$ ($T_c \sim 0.7$ K) [1], a great deal of interest is attracted to the intricate physics of strongly correlated electron systems. Up to now, it has been established that the superconductivity in Ce-based HF compounds occurs close to the magnetic instability. In a stoichiometric $CeCu_2Si_2$ at ambient pressure, it is now believed that the superconducting (SC) phase is embedded in another phase denoted as *A* phase. This *A* phase, which was shown to be in magnetic origin first by NMR [2] and then by subsequent muon spin rotation (μSR) [3] measurements, was ensured by elastic and thermal expansion experiments on a high-quality single crystal [4]. The NMR experiments revealed that the NQR intensity observed at about 3.435 MHz decreases upon cooling below $T_m \sim 1$ K without any NQR spectral broadening associated with spontaneous magnetic moments [2,5]. This result implies that magnetic correlations with a certain wave number $\mathbf{Q}$ develop rapidly below T_m and then its characteristic frequency $\Gamma_{\mathbf{Q}}(T)/\hbar \equiv \omega_{\mathbf{Q}}$ approaches NMR/NQR frequencies ω_N due to a large enhancement of $\chi_{\mathbf{Q}}(T)$, because $1/T_1 \propto \omega_{\mathbf{Q}}/(\omega_{\mathbf{Q}}^2 + \omega_N^2)$ and $1/T_2 \propto \chi_{\mathbf{Q}}(T)$. The *A* phase should be distinguished from a static magnetic order (SMO), but characterized by magnetic correlations fluctuating with low frequencies comparable to ω_N [5]. This dynamical aspect of the *A* phase is consistent with recent μSR experiments [6]. The lack of SMO seems to be supported by the fact that all attempts at direct observation of the magnetic structure by neutron diffraction (ND) have failed so far [7].

One may expect that the *A* phase has a common feature to unusual "antiferromagnetic (AF) order" below $T_N = 5$ K in UPt_3 detected by the ND [8]. No NMR anomalies, however, were ever detected in UPt_3 [9,10]. Recently, Okuno and Miyake proposed that UPt_3, exhibiting the mysterious behaviors in the AF order, is in the *spin-density wave (SDW) state* oscillating with finite frequencies ($\omega_{\mathbf{Q}}$) larger than those of the NMR frequency ($\omega_N \sim 10^{6\sim7}$ Hz) and smaller than those of the ND ($\omega_{\mathrm{ND}} \sim 10^{11\sim12}$ Hz) [11].

A series of polycrystal $Ce_xCu_{2+y}Si_2$ in the vicinity of stoichiometric composition as well as a high-quality single crystal have been studied thoroughly by means of resistivity, specific-heat, μSR, elastic constant, and dilatation measurements [4,6,12–15]. It was found that both the *A* and SC phases are extremely sensitive to sample preparation, especially to a Ce-nominal content *x* [14], and that these two phases are nearly degenerate [4]. The *A* phase was furthermore suggested to be expelled below T_c under zero field due to the onset of superconductivity in both the high-quality single [4] and polycrystal samples [14]. Quite recently, macroscopic measurements have revealed that $CeCu_2Si_2$ is located in the vicinity of a quantum critical point [15]. In order to highlight an interplay between the *A* and SC phases and to clarify an evolution of ground state with varying the Ce-nominal content *x* from a microscopic point of view, we have made Cu-NQR studies on the same series of $Ce_xCu_{2+y}Si_2$ polycrystal samples used in the previous measurements [6,12,14,15].

We used four samples with different Ce-nominal content such as $CeCu_{2.05}Si_2$ with $T_c \sim 0.7$ K (hereafter denoted as Ce1.00), $Ce_{1.025}Cu_2Si_2$ with $T_c \sim 0.6$ K (Ce1.025), $Ce_{0.99}Cu_{2.02}Si_2$ (Ce0.99), and nonsuperconducting $Ce_{0.975}Cu_2Si_2$ (Ce0.975). We should remark that the ground state in the four samples depends not on off-stoichiometry in Cu content *y* but mainly on Ce content *x*, since the T_c in $CeCu_{2+y}Si_2$ ($-0.01 \le y \le 0.2$) is in the narrow range between 0.6 K ($CeCu_{1.99}Si_2$) and 0.65 K ($CeCu_{2.2}Si_2$) [16]. Detailed preparation of samples was reported elsewhere [14]. The x-ray diffraction pattern does not show any difference for all of the compounds, ensuring that the lattice parameter is independent of *x*. Although the small diamagnetic signal was observed at $T_c \sim 0.6$ K

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in Ce0.99, the absence of sharp anomalies at T_c in the specific-heat and the thermal expansion data are indicative of its nonbulk nature on the SC transition. All of the samples were moderately crushed into powder with diameters larger than 100 μm in order to avoid some crystal distortion if any.

The NQR frequency $\nu_{NQR} = \omega_N/2\pi$ ($\sim$3.435 MHz) is confirmed to be independent of x. Full width at half maximum (FWHM) in Cu-NQR spectrum, which depends on crystal homogeneity, is estimated to be 26, 13, 14, and 35 kHz for Ce1.025, Ce1.00, Ce0.99, and Ce0.975, respectively. The FWHM is about twice as large for Ce1.025 and Ce0.975 than for Ce1.00 and Ce0.99; however, a maximum value of FWHM $\sim$35 kHz for Ce0.975 is even smaller than $\sim$40 and $\sim$150 kHz reported in Refs. [17] and [18]. We note that the FWHM $\sim$13 kHz (14 kHz) for Ce1.00 (Ce0.99) is comparable to 11 kHz for the single crystal, ensuring the high quality of Ce1.00 and Ce0.99 in a microscopic level.

We now remark on the anomalies relevant to the A phase. Figure 1 displays the T dependence of NQR intensity (I) multiplied by temperature (T), $I \times T$ normalized by $I \times T$ at 4.2 K for all of the samples. $I \times T$ decreases rapidly below T_c due to the SC diamagnetic shielding of rf field, whereas it is also clear that $I \times T$ starts to decrease below T_m far above T_c. Since $I(\tau)$ depends on a pulse interval (τ) between two pulses by means of the spin-echo method, $I(0)$ is evaluated through the relation of $I(\tau) = I(0)\exp(-2\tau/T_2)$ where $1/T_2$ is the spin-echo decay rate. T_m is estimated as 0.8, 1, 1.2, and 1 K for Ce1.025, Ce1.00, Ce0.99, and Ce0.975, respectively. The μSR measurements on the same samples detected the A phase below T_m dominated by very slow magnetic fluctuations ($\sim$3 MHz) close to the NQR frequency and a coexistence with the paramagnetic region where frequencies of magnetic fluctuations remain over a higher frequency range [6]. The SC volume fractions at T_c are considered to be proportional to the paramagnetic region by comparison with the specific-heat results [6]. The marked reduction in $I \times T$ without any spectral broadening is therefore due to the emergence of the A phase. Note that the decrease in $I \times T$ upon cooling is ascribed to an extraordinary short T_1 and/or T_2 in the A phase, which is estimated to be $\sim$0.14 μsec from the very slow fluctuations ($\sim$3 MHz).

On the other hand, as shown in Fig. 2, both ^{63,65}Cu-NQR spectral widths increase in Ce0.975 below 0.6 K, which gives evidence for an onset of static magnetic order (SMO). Provided that possible magnetic structure in Ce0.975 is of an antiferromagnetic type with a wave vector $\mathbf{Q} = (1/2, 1/2, c)$ in $CePd_2Si_2$ and $CeRh_2Si_2$ or with $\mathbf{Q} = (0, 0, 1/2)$ in URu_2Si_2, hyperfine fields are canceled out at the Cu sites occupying a magnetically symmetric position. Therefore either such a helical structure as in $CeCu_2Ge_2$ or some SDW may be realized [19]. The increase of FWHM proportional to spontaneous moment M_s is close to a mean-field type below $T_N = 0.6$ K. A rough estimate of M_s from the FWHM at low T gives rise to $0.05\mu_B$ per Ce ion by assuming the hyperfine coupling constant $A_{hf} = -4.6$ kOe$/\mu_B$ [20]. We note that this SMO coexists with the A phase below $T_N \sim 0.6$ K, because the value of $I \times T$ below T_m remains reduced, as seen in Fig. 1.

Next, in order to demonstrate an evolution of the ground state from the magnetically ordered to the SC state in a series of $Ce_xCu_{2+y}Si_2$ compounds, we show the T dependence of $1/T_1$ of ^{63}Cu under zero field for all of the samples in Fig. 3. $1/T_1$ is determined by a single component, except for the T_1 data below 1 K in Ce0.975 where long (T_{1L}) and short (T_{1S}) components are estimated tentatively. Above 3 K, $1/T_1$'s for all of the samples fall on

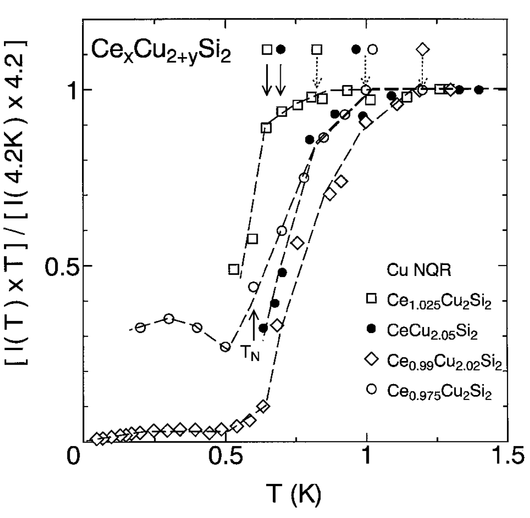

FIG. 1. T dependence of the Cu-NQR intensity multiplied by temperature, $I \times T$ normalized by $I \times T$ at 4.2 K. Dotted and solid arrows indicate T_m and T_c, respectively.

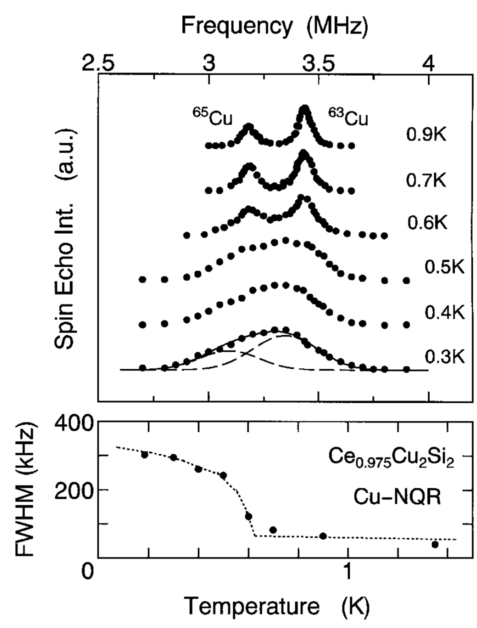

FIG. 2. T dependence of ^{63,65}Cu-NQR spectrum in $Ce_{0.975}$-Cu_2Si_2. The bottom figure shows the T dependence of the FWHM for the ^{63}Cu-NQR spectrum.

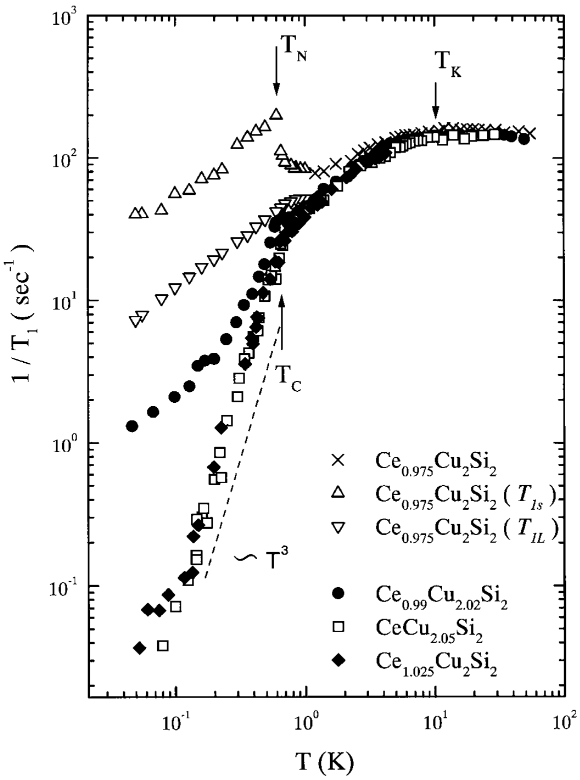

FIG. 3. T dependence of $1/T_1$ in $Ce_xCu_{2+y}Si_2$. Above 1 K, the T_1 in $Ce_{0.975}Cu_2Si_2$ is determined by a single component. Below 1 K, short (T_{1S}) and long (T_{1L}) components of $1/T_1$ are presented.

the same curve regardless of varying x. It is experimentally known that a constant value of $1/T_1$ starts to decrease below T_K. $T_K \sim 10$ K is hence nearly independent of Ce concentration x. Below 2 K, the T dependence of $1/T_1$ reflects the difference in the ground state of each compound. A clear peak in $1/T_{1S}$ for Ce0.975 is observed at $T_N = 0.6$ K due to critical magnetic fluctuations towards the SMO.

By contrast, the $1/T_1$ for Ce1.025 exhibits a linear-T decrease below 1.2 K (denoted as T_F), probing the formation of heavy-fermion band. It is confirmed from the present NQR, the μSR [6], and the specific-heat [12,14] measurements that the anomalies relevant to the A phase below T_m are much more pronounced for Ce1.00 than for Ce1.025. It should, however, be noted that $1/T_1$'s in the SC state for Ce1.025 and Ce1.00 follow a T^3 dependence in the T range of 0.6–0.1 K, falling on a single line. This result suggests that the A phase is expelled below T_c by the onset of SC phase, which is consistent with the result by elastic measurement on the high-quality single crystal [4].

In Ce0.99, as seen in Fig. 1, the $I \times T$ at 0.012 K reduces to ~5% of the value at 4.2 K without any trace of SMO. This proves that the A phase remains dominated by slow magnetic fluctuations comparable to ω_N down to 0.012 K. In this context, the A phase should be characterized as "critical magnetic phase" (CMP). The fact that the NQR spectrum is yet visible below T_m demonstrates a contamination of "paramagnetic domain" (PD) characterized by magnetic fluctuations with much higher frequencies than ω_N. $1/T_1$ for the PD state decreases gradually with decreasing T, followed by a small hump at about 0.6 K. With further decreasing T below 0.6 K, the small SC diamagnetization emerges associated with an onset of SC in the PD. Correspondingly, $1/T_1$ decreases steeply below 0.6 K and exhibits a similar T variation to $(1/T_{1L})$ in Ce0.975 below 0.3 K. Thus *the SC characteristics for the PD are not the same as those in the bulk SC phase for Ce1.00 and Ce1.025*. We note that the SC phase contained in Ce0.99 is significantly affected by the low-lying magnetic excitations of thermally excited quasiparticles. The sample of Ce0.99 reveals the magnetic criticality at the border to both the magnetic and SC phases.

On the basis of these rich outcomes from the NQR study, we propose a schematic view on dynamical magnetic response function in Fig. 4. In the figure, the q averaged imaginary part of dynamical susceptibility $\sum_q \times \chi''(q,\omega) \equiv \chi''(\omega)$ is schematically depicted as the function of frequency of magnetic correlations ω. Near 3 K, the spectral weight (SPW) of $\chi''(\omega)$ is distributed over ω from 0 to $\omega_K = k_B T_K/\hbar$ ($T_K \sim 10$ K) for all of the samples, as in Fig. 4a. We note that the SPW for the CMP develops at about $\omega_{\mathbf{Q}} \sim \omega_N$ below T_m. In Ce1.025 and Ce1.00, as shown in Fig. 4b, once these SPW's develop below T_m, they are totally transferred into a frequency range above $\omega_s = \Delta_s/\hbar$ at $T \rightarrow 0$ (Fig. 4c). Here Δ_s is the SC energy gap. Note that an intensity of SPW at about $\omega_{\mathbf{Q}} \sim \omega_N$ reflects a fraction of the CMP. A larger intensity of

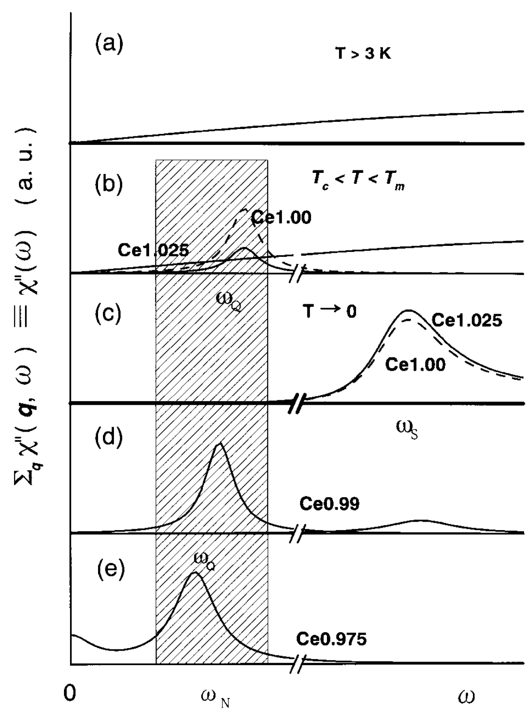

FIG. 4. Schematic figures of the frequency dependence of the q averaged imaginary part of dynamical susceptibility in $Ce_xCu_2Si_2$ (see text).

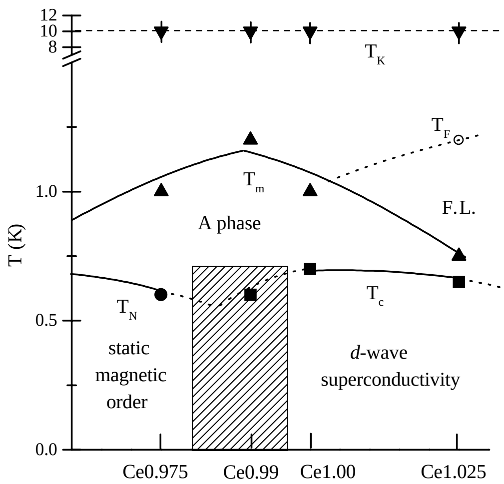

FIG. 5. Schematic phase diagram in $Ce_xCu_2Si_2$. T_K is the Kondo temperature. T_N and T_c are the magnetic and SC transition temperatures, respectively. T_m is the temperature below which $I \times T$ starts to decrease. T_F is the temperature below which T_1T = const relation holds. The region denoted by slanted lines is the critical region where the static magnetic order crosses over to the unconventional superconductivity.

SPW in Ce1.00 than in Ce1.025 is because $I \times T$ proportional to a fraction of the PD is smaller for the former than for the latter. In Ce0.99, the SPW for the CMP at about $\omega_{\mathbf{Q}} \sim \omega_N$ grows markedly below $T_m \sim 1.2$ K and remains dominant down to 0.012 K. A small fraction of the PD gives rise to the minor SC phase below 0.6 K. Therefore, a tiny SPW (5% of the total) is present in a frequency range higher than $\omega_{\mathbf{Q}}$, as in Fig. 4d. Thus the dominant CMP coexists with the SC phase. In Ce0.975, a tiny saturation moment $M_s \sim 0.05\mu_B$ in the SMO below $T_N = 0.6$ K means that the small SPW peaks at $\omega = 0$, as indicated in Fig. 4e. In addition, considerable SPW remains finite at about $\omega_{\mathbf{Q}} \sim \omega_N$.

One question is what is the role played by the 1% Ce-nominal deficiency (Ce0.99) introduced into Ce1.00. An evolution of the SC to the SMO has been found in the 2% Ge-substituted sample for the Si sites which decreases the T_K to ~8 K [21], whereas the magnetic character of Ce0.99 is changed into a type of Ce1.025 by applying the pressure $p = 0.7$ GPa which increases the T_K [15]. It is possible that the strength of the hybridization between $4f$ and conduction electrons is much more finely tuned by varying Ce-nominal content than by the Ge substitution [15].

By contrast, Fukuyama [22] and Kohno *et al.* [23] have recently pointed out from a different context that, once the disorder associated with a nominal Ce deficiency is introduced, the SMO or the CMP at finite T is nucleated around the impurities in the singlet ground state, i.e., the SC phase in the present case. We note, however, that the disorder does not always stabilize the CMP, since the magnetic anomalies associated with the CMP are less pronounced in Ce1.025 than in Ce0.99, although the microscopic disorder is more distinctly introduced into the former rather than into the latter. If a Ce deficiency in Ce0.99 acted as a spin defect, this scenario would be promising, as also thought implicitly [22,23]. In order to settle this issue, we need further systematic studies on the x and pressure dependences of the CMP.

In conclusion, we present in Fig. 5 the phase diagram in a series of $Ce_xCu_2Si_2$ compounds by varying the Ce-nominal content x. We found the evolution of the ground state from the SMO (Ce0.975) to the SC (Ce1.025) at ambient pressure. The ground state in Ce0.99 is dominated down to 0.012 K by slow magnetic fluctuations comparable to the NQR frequency ω_N. This state, referred to as the critical magnetic phase, in place of the A phase, coexists with the SC phase of a tiny fraction. The emergence of the AF phase or the CMP at finite T out of the singlet SC state seems to be quite ubiquitous in strongly correlated superconductivity next to the AF phase.

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[1] F. Steglich *et al.,* Phys. Rev. Lett. **43**, 1892 (1979).
[2] H. Nakamura *et al.,* J. Magn. Magn. Mater. **76–77**, 676 (1988); J. Phys. Condens. Matter **4**, 473 (1992).
[3] Y. J. Uemura *et al.,* Phys. Rev. B **39**, 4726 (1989); G. M. Luke *et al.,* Phys. Rev. Lett. **73**, 1853 (1994).
[4] G. Bruls *et al.,* Phys. Rev. Lett. **72**, 1754 (1994).
[5] Y. Kitaoka *et al.,* J. Phys. Soc. Jpn. **60**, 2122 (1992).
[6] R. Feyerherm *et al.,* Physica (Amsterdam) **206B–207B**, 596 (1995); Phys. Rev. B **56**, 699 (1997).
[7] J. Flouquet *et al.* (private communication).
[8] G. Aeppli *et al.,* Phys. Rev. Lett. **63**, 676 (1989).
[9] H. Tou *et al.,* Phys. Rev. Lett. **77**, 1374 (1996); **80**, 3129 (1998).
[10] Recently the marked reduction of the $I \times T$ of Pt-NMR in UPt_3 has been observed without any spectral broadening below 50 mK, where the specific-heat and the ND experiments suggested an onset of some long-range magnetic order.
[11] Y. Okuno and K. Miyake, J. Phys. Soc. Jpn. **67**, 3342 (1998).
[12] F. Steglich *et al.,* J. Phys. Condens. Matter **8**, 9909 (1996).
[13] I. Sheikin *et al.,* J. Phys. Condens. Matter **10**, 749 (1998).
[14] R. Modler *et al.,* Physica (Amsterdam) **206B–207B**, 586 (1995).
[15] P. Gegenwart *et al.,* Phys. Rev. Lett. **81**, 1501 (1998).
[16] Y. Onuki *et al.,* J. Phys. Soc. Jpn. **56**, 1454 (1987).
[17] Y. Kitaoka *et al.,* J. Phys. Soc. Jpn. **55**, 723 (1987).
[18] C. Tien, Phys. Rev. B **43**, 83 (1991).
[19] G. Knopp *et al.,* Z. Phys. B **77**, 95 (1989).
[20] K. Ueda *et al.,* J. Phys. Soc. Jpn. **56**, 867 (1987).
[21] K. Ishida *et al.* (unpublished).
[22] H. Fukuyama, cond-mat/9812294 (to be published).
[23] H. Kohno, H. Fukuyama, and M. Sigrist, J. Phys. Soc. Jpn. **68**, 1500 (1999).