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Itinerant electron metamagnetism in $LaCo_9Si_4$

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The strongly exchange enhanced Pauli paramagnet $LaCo_9Si_4$ is found to exhibit an itinerant metamagnetic phase transition with indications for metamagnetic quantum criticality. Our investigation comprises magnetic, specific heat, and nuclear magnetic resonance measurements as well as *ab initio* electronic structure calculations. The critical field is about 3.5 T for $H||c$ and 6 T for $H\perp c$, which is the lowest value ever found for rare earth intermetallic compounds. In the ferromagnetic state there appears a moment of about 0.2 μ_B/Co at the 16*k* Co-sites, but significantly smaller moments at the 4*d* and 16*l* Co-sites.

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Reports on superconductivity on the border of itinerant electron ferromagnetism in UGe_2 and $ZrZn_2$[1,2] attracted considerable interest on quantum critical phenomena in ferromagnetic materials and motivated the search for new materials which are in the vicinity of a ferromagnetic (FM) quantum critical point at ambient pressure. A fascinating system which may fit in this scenario is the solid solution $LaCo_{13-x}Si_x$ where ferromagnetism vanishes near the stoichiometric composition $LaCo_9Si_4$ (see Refs. 3–5). Notwithstanding the qualitative agreement between the initial reports there have been rather inconsistent results for the Curie temperature of $LaCo_9Si_4$ with $T_C \simeq 900$ K and $T_C \simeq 40$ K in Refs. 3,5. Our reinvestigation of $LaCo_{13-x}Si_x$ in the vicinity of the stoichiometric 1-9-4 composition revealed a monotonous decrease of the Curie temperature with $T_C \simeq 79$ K and 36 K for $x=3.8$ and 3.9, respectively, and the absence of FM order in well annealed single phase $LaCo_9Si_4$.[6]

In this Communication we show a full crystallographic characterization of the true ternary compound $LaCo_9Si_4$ and present convincing evidence for a magnetic instability at relatively low fields of a few Tesla, namely, the occurrence of itinerant electron metamagnetism (IEMM).

Polycrystalline samples $LaCo_9Si_4$ were synthesized by high-frequency induction melting of metal ingots (La 4N, Co 4.5N, and Si 6N) and subsequent heat treatment at 1050 °C for 10 days. The phase purity and composition has been verified by electron microprobe studies. The room-temperature structure investigation has been performed on a small single crystal ($56\times72\times56$ μm^3) on a four circle Nonius Kappa diffractometer equipped with a CCD area detector. 430 reflections $>4\sigma(F_0)$ out of 480 have been used for the structure refinement. All details of the applied methodology were recently summarized in context with our structure investigation on Ce- and $LaNi_9Si_4$.[7] Analogous to $LaNi_9Si_4$ single crystal x-ray diffraction reveals for stoichiometric $LaCo_9Si_4$ a fully ordered tetragonal $LaFe_9Si_4$-type structure[8] ($NaZn_{13}$—derivative with *space group* $I4/mcm$). The occupancies of all crystallographic sites have been refined but did not reveal any significant deviations from stoichiometry. Refining anisotropic thermal displacement factors in the final run yielded *R* values as low as 0.02 confirming the structural model with full atom order. The results of the structure determination are summarized in Table I. Being a fully ordered ternary compound $LaCo_9Si_4$ takes an exceptional position within the solid solution $LaCo_{13-x}Si_x$ which is corroborated by the residual resistivity values showing a clear minimum at $x=4$ with $\rho_0 \simeq 17$ $\mu\Omega$ cm (see Ref. 6) and by the limited solid solubility just around the stoichiometric composition where small off-stoichiometries, e.g., $x=4.05$ or $x=3.95$ yielded inhomogeneous samples with secondary phases.

The observation of FM order in $LaCo_{13-x}Si_x$ approaching zero temperature approximately at the stoichiometric composition 1-9-4 suggests that $LaCo_9Si_4$ may be at or nearby a FM quantum critical point. This is supported by a rather

TABLE I. X-ray single crystal data for $LaCo_9Si_4$; space group $I4/mcm$; No. 140.

Atom	Wyckoff position	Coordinates
	$a=0.7833(1)$ nm; $c=1.15657(2)$ nm	
La	4*a*	$(0,0,\frac{1}{4})$
Co(1)	16*k*	$(x,y,0)$
		$x=0.06957(6)$; $y=0.20078(5)$
Co(2)	16*l*	$(x,x+\frac{1}{2},z)$
		$x=0.62708(4)$; $z=0.17994(4)$
Co(3)	4*d*	$(0,\frac{1}{2},0)$
Si	16*l*	$(x,x+\frac{1}{2},z)$
		$x=0.17013(8)$; $z=0.12080(8)$

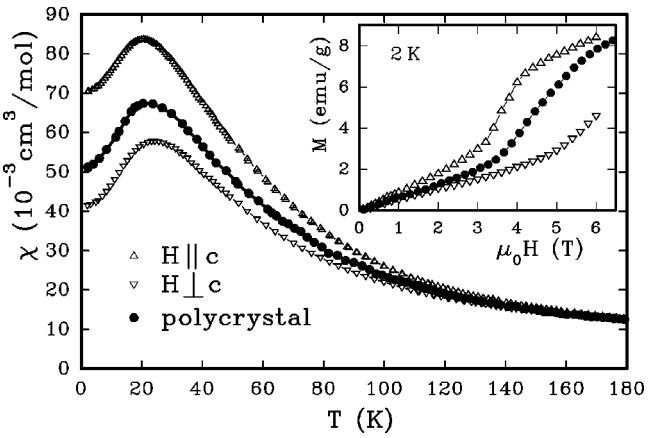

FIG. 1. dc magnetic susceptibility of $\chi(T)$ of $LaCo_9Si_4$ measured at 1 T on a large randomly oriented polycrystalline sample (filled symbols) and on a c axis oriented textured specimen with $H||c$ and $H\perp c$ (open symbols); inset: the corresponding isothermal magnetization curves $M(H)$ measured at 2 K.

large Sommerfeld value $\gamma \simeq 200$ mJ/mol K^2 of $LaCo_9Si_4$ which is the maximum value within the solid solution. The temperature dependencies of the electrical resistivity and magnetic susceptibility measured in external magnetic fields $\mu_0 H < 3$ T in fact indicate a spin fluctuation regime.[6] The dc magnetic susceptibility $\chi(T)$ shown in Fig. 1 exhibits a pronounced maximum at about 20 K. The low-temperature susceptibility χ_0 of a large randomly oriented polycrystalline sample measured with a vibrating sample magnetometer (VSM) at 1 T (filled symbols in Fig. 1) amounts to $\chi_0 \simeq 0.051$ cm^3/mol. Superconducting quantum interference device (SQUID) measurements performed on small c axis oriented textured specimens (<1 mg) reveal a significant anisotropy of the paramagnetic susceptibility yielding $\chi_0(H||c) \sim 0.07$ cm^3/mol and $\chi_0(H\perp c) \simeq 0.04$ cm^3/mol (open symbols in Fig. 1).

The isothermal magnetization $M(H)$ measured on a bulk polycrystal $LaCo_9Si_4$ in a 15 T VSM is shown in Fig. 2(a) and as Arrott plots (M^2 vs H/M) in Fig. 2(b). The 2 K and 20 K results indicate IEMM, i.e., a phase transition to a field induced FM state at $\mu_0 H_c \sim 3$–6 T with a typical S shape of the Arrott plot. The absence of any hysteretic behavior (within the resolution of both, VSM and SQUID) indicates that the transition is on the verge to second order and may be connected with the vicinity to a field induced quantum critical point. The extrapolated ''spontaneous'' magnetization of the field induced FM state M_0 is about 0.9 μ_B/f.u. [see the dotted line in Fig. 2(b) yielding $M_0^2 \sim 0.8(\mu_B/\text{f.u.})^2$]. The considerable width of the metamagnetic critical field $\mu_0 H_c \sim 3$–6 T obtained on a polycrystalline sample is due to the random orientation of crystallites with respect to the external magnetic field. For oriented crystals the IEMM transition is observed at about 3–4 T for $H||c$ and near 6 T for $H\perp c$ (see inset of Fig. 1), i.e., the metamagnetic critical fields are inversely proportional to the corresponding susceptibilities $\chi_0(H||c)$ and $\chi_0(H\perp c)$. The almost infinite initial slope of the Arrott plot at 30 K indicates the upper temperature limit of IEMM.

The specific heat of polycrystalline $LaCo_9Si_4$ measured in

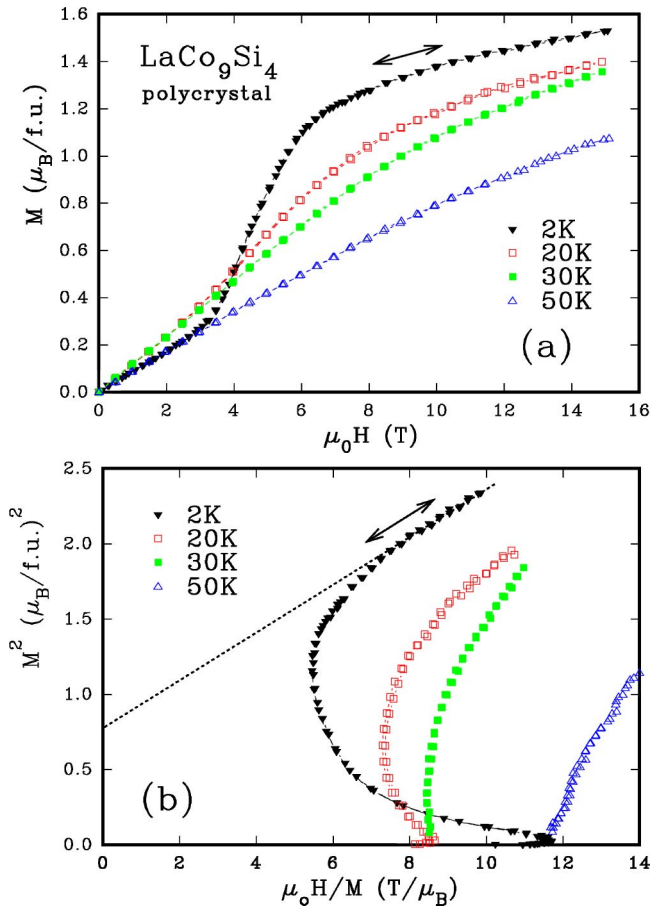

FIG. 2. (Color online) (a) Isothermal magnetization $M(H)$ of polycrystalline $LaCo_9Si_4$; (b) Arrott plot: M^2 vs H/M.

external magnetic fields up to 10 T (see Fig. 3) reveals an initial increase of the electronic specific-heat coefficient γ from 200 mJ/mol K^2 at zero field to a maximum value of above 230 mJ/mol K^2 at 5.3 T. Upon further increasing the magnetic field there is a significant reduction of the γ value down to about 190 mJ/mol K^2 at 10 T. The direct measurement of the magnetocaloric effect at about 3 K (not shown for brevity) where $\Delta T(H)$ [approximately proportional to $-\Delta S(H)$] reveals a state of maximum entropy at 5.3 T

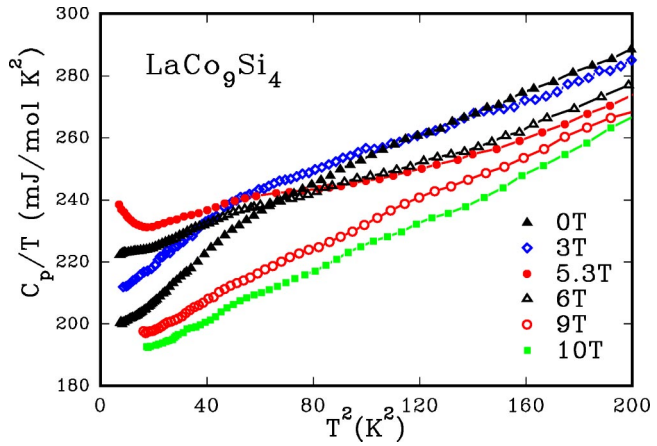

FIG. 3. (Color online) Temperature dependent specific heat $C_p(T)$ of $LaCo_9Si_4$ displayed as C/T vs T^2.

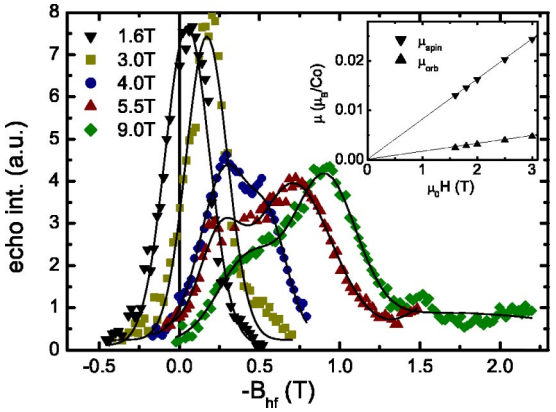

FIG. 4. (Color online) NMR spin echo amplitude of $LaCo_9Si_4$ powder at 7.5 K vs negative B_{hf} for various applied fields as labeled; inset: spin and orbital moments below the critical field, for higher field this evaluation becomes impossible (see text).

which defines a thermodynamic critical field $\mu_0 H_c^T \simeq 5.3$ T of the polycrystal being in close agreement with the weighted mean of $\frac{1}{3}\mu_0 H_c||c + \frac{2}{3}\mu_0 H_c \perp c \simeq 5.2$ T. The superposition of specific-heat contributions of randomly oriented crystallites inhibits a straightforward analysis of the thermodynamic features of the critical state. Nevertheless it is noteworthy that below about 3 K a low-temperature upturn develops in C/T just at $\mu_0 H_c^T = 5.3$ T being indicative for quantum criticality which may of course be limited to areas or spots on the Fermi surface. Similar observations indicating metamagnetic quantum criticality have been reported for $CeRu_2Si_2$ and $Sr_3Ru_2O_7$ (see, e.g., Refs. 9,10) which is remarkable because of the distinctly different mechanisms involved in each of these cases.

The ^{59}Co nuclear magnetic resonance (NMR) spin-echo spectra of $LaCo_9Si_4$ at 7.5 K have been measured in external fields between 1.5 and 9 T. Neglecting dipolar and transferred field contributions the resonance frequency f is determined by $f/\gamma = B_{hf} + \mu_0 H$, where $\gamma = 10.1$ MHz/T is the gyromagnetic ratio of ^{59}Co and B_{hf} is the hyperfine field due to a magnetic moment μ in the electronic shell of the nucleus. Figure 4 shows that even below the IEMM transition the considerable inhomogeneous line width of $\Delta B_{hf} = 0.25$ T due to induced moments does not allow to resolve the three crystallographic sites. At $\mu_0 H \geqslant 3.5$ T a drastic line broadening indicates the IEMM and the spectrum develops an unresolved splitting into two lines with a broad shoulder to high internal fields. The inhomogeneous broadening of the transition in the field range up to 6 T is consistent with the magnetic anisotropy discussed above. For $\mu_0 H \geqslant 6$ T the shape of the spectrum becomes again independent of the external field with a low intensity line at $-B_{hf} \simeq 0.22$ T, a line of roughly three times this intensity at $-B_{hf} \simeq 0.75$ T, and a broad shoulder in the range $-B_{hf} \sim 1$–2.3 T. From the line intensities and the band-structure calculations discussed below we tentatively assign these structures to $4d$, $16l$, and $16k$ Co, respectively.

Below the IEMM transition we estimate the mean Co spin and orbital moment μ_{spin} and μ_{orb} from B_{hf} and the total magnetization (Fig. 2) by solving $B_{hf} = \alpha\mu_{spin} + \beta\mu_{orb}$ and $\mu = \mu_{spin} + \mu_{orb}$ with hyperfine coupling constants $\alpha = -12$ T/μ_B, $\beta = 65$ T/μ_B.[11] The result of this evaluation is shown in the inset of Fig. 4 revealing a constant spin susceptibility of $9 \times 10^{-3}\,\mu_B$/T Co and an orbital contribution of about $1.5 \times 10^{-3}\,\mu_B$/T Co. This decomposition becomes impossible with the line broadening and unresolved splitting at higher field due to the unknown Co sublattice magnetizations. Under the assumption of equal ratio μ_{spin}/μ_{orb} for all Co-sites we find with the line assignment above sublattice moments at 9 T of 0.18, 0.09, and 0.04 μ_B/Co at $16k$, $16l$, and $4d$ sites, respectively.

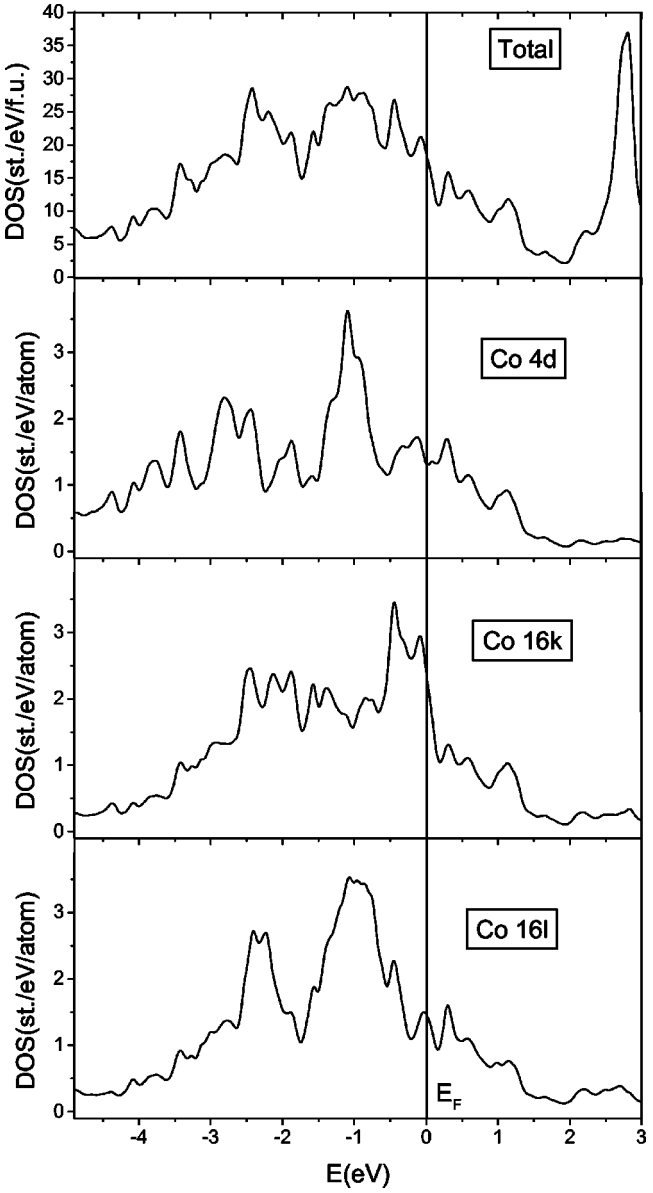

FIG. 5. Electronic density of states per unit cell (total) and atom projected for the three different Co sites of $LaCo_9Si_4$.

The *ab initio* electronic structure calculations were performed employing the full-potential linear-augmented-plane-wave method.[12] The effects of exchange and correlation were treated within the local density-functional formalism including the general gradient approximation.[13] The Brillouin zone integration was performed for 216 **k** points to achieve self consistency and for 1728 **k** points to determine the density of

states (DOS) given in Fig. 5 which shows the total DOS and the site projected DOS for the 3 different Co sites. From the total DOS it can be seen that the Fermi energy (E_F) lies in a strongly falling flank of a pronounced peak. Such a feature is known to be a necessary requirement for the occurrence of a metamagnetic phase transition.[14] This peak in the total DOS stems from the contribution by the Co atoms at the 16*k* position, where the DOS at E_F is so large to roughly fulfill the Stoner criterion. For the two other Co positions the DOS at E_F is significantly lower. The Co atoms at the 16*k* positions form planes within the crystal structure which are separated from each other by almost nonmagnetic *spacers* causing a narrowing of the *d* band. To study the metamagnetic behavior fixed spin moment calculations were performed in the same fashion as it was done for YCo_2 earlier.[15] At the experimental lattice constant we obtain a ferromagnetically ordered ground state. At slightly reduced volume a metamagnetic behavior develops. The magnetic moments obtained in the IEMM state are 0.3, 0.07, and 0.02 μ_B/Co at 16*k*, 16*l*, and 4*d* sites, respectively, in fair agreement with the experiments. The total energy vs magnetic moment curves show the typical behavior like the archetypal itinerant metamagnet YCo_2.[15]

The total DOS of $LaCo_9Si_4$ shown in Fig. 5 yields at E_F about 19 states/eV f.u. which implies a *T*-linear specific contribution $\gamma_b \sim 45\,\mathrm{mJ/mol\,K^2}$. The latter value is just about one fourth of the experimental value, $\gamma \simeq 200\,\mathrm{mJ/mol\,K^2}$, revealing a spin-fluctuation mass enhancement $\lambda_{spin} \sim 3.3$ which indicates strongly exchange enhanced Pauli paramagnetism. The mass enhancement of about three is also in line with the observed instability towards itinerant ferromagnetism and compares well with related IEMM systems like YCo_2, however, with a significantly smaller critical field in the case of $LaCo_9Si_4$ which is the lowest value ever found for rare earth intermetallic compounds.

To summarize, $LaCo_9Si_4$ is a true ternary compound with a fully ordered tetragonal $LaFe_9Si_4$-type structure which exhibits itinerant electron metamagnetism with an anisotropic critical field $\mu_0 H_c || c \sim 3.5$ T and $\mu_0 H_c \perp c \sim 6$ T. The anisotropy of the latter is in clear correspondence with the anisotropy of the paramagnetic susceptibility and arises from small but finite Co-orbital moments resolved by NMR. Both the band-structure calculations and NMR reveal significantly different contributions from the three Co sites where Co at the 16*k* positions are found to be responsible for the metamagnetic transition. This phase transition appears to be on the verge to second order and may be connected with a field induced quantum critical point. The vicinity to quantum criticality is supported by the magnetocaloric effect revealing an entropy maximum just at the critical field of 5.3 T (for bulk specimens) together with a small low-temperature upturn of C/T at H_C^T, which resembles the metamagnetic criticality of $CeRu_2Si_2$ and $Sr_3Ru_2O_7$. Despite the differences in spin and electronic dimensionality common trends emerge as described by Millis *et al.*[16] for metamagnetic quantum criticality: the finite-temperature peak in the susceptibility, the maximum of entropy and γ at the critical field and the paramagnetic ground state that should, according to band-structure calculations, be ferromagnetic. Accordingly, $LaCo_9Si_4$ and related novel intermetallics with 1-9-4 stoichiometry are fascinating systems to study the interrelations of spin fluctuation behavior, IEMM, and quantum criticality in structures with full translational symmetry. They might be promising candidates to search for the appearance and/or coexistence of superconductivity and itinerant electron ferromagnetism.

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[1] S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthough, G.G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, and J. Flouquet, Nature (London) **406**, 587 (2000).

[2] C. Pfleiderer, M. Uhlarz, S.M. Hayden, R. Vollmer, H.v. Löhneysen, N.R. Bernhoeft, and G.G. Lonzarich, Nature (London) **412**, 58 (2001).

[3] G.H. Rao, J.K. Liang, Y.L. Zhang, X.R. Cheng, and W.H. Tang, Appl. Phys. Lett. **64**, 1650 (1994).

[4] G.H. Rao, J.K. Liang, Y.L. Zhang, X.R. Cheng, W.H. Tang, and C. Dong, Phys. Rev. B **51**, 60 (1995).

[5] M.Q. Huang, W.E. Wallace, R.T. Obermyer, S. Shimizu, M. McHenry, and S.G. Sankar, J. Appl. Phys. **79**, 5949 (1996).

[6] M. El-Hagary, H. Michor, M. Wind, E. Bauer, G. Hilscher, and P. Rogl, in Proceedings of the 8th International Conference on Crystal Chemistry of Intermetallic Compounds, L'viv, Ukraine 2002 [J. Alloys Compd. (to be published)].

[7] H. Michor, St. Berger, M. El-Hagary, C. Paul, E. Bauer, G. Hilscher, P. Rogl, and G. Giester, Phys. Rev. B **67**, 224428 (2003).

[8] W.H. Tang, J.K. Liang, X.L. Chen, and G.H. Rao, J. Appl. Phys. **76**, 4095 (1994).

[9] J. Flouquet, P. Haen, S. Raymond, D. Aoki, and G. Knebel, Physica B **319**, 251 (2002).

[10] R.S. Perry, L.M. Galvin, S.A. Grigera, L. Capogna, A.J. Schofield, A.P. Mackenzie, M. Chiao, S.R. Julian, S. Ikeda, S. Nakatsuji, Y. Maeno, and C. Pfleiderer, Phys. Rev. Lett. **86**, 2661 (2001); S.A. Grigera, R.S. Perry, A.J. Schofield, M. Chiao, S.R. Julian, G.G. Lonzarich, S.I. Ikeda, Y. Maeno, A.J. Millis, and A.P. Mackenzie, Science **294**, 329 (2001).

[11] R.L. Streever, Phys. Rev. B **19**, 2704 (1979).

[12] E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, Phys. Rev. B **24**, 864 (1981); H.J.F. Jansen and A.J. Freeman, *ibid.* **30**, 561 (1984).

[13] Y. Wang and J.P. Perdew, Phys. Rev. B **44**, 13 298 (1991).

[14] P.R. Rhodes and E.P. Wohlfarth, Proc. R. Soc. London **273**, 247 (1963).

[15] K. Schwarz and P. Mohn, J. Phys. F: Met. Phys. **14**, L128 (1984).

[16] A.J. Millis, A.J. Schofield, G.G. Lonzarich, and S.A. Grigera, Phys. Rev. Lett. **88**, 217204 (2002).