PHYSICAL REVIEW B **70**, 220406(R) (2004)

Pressure-induced magnetic phase transition in gold-phase SmS

Y. Haga,[1,2] J. Derr,[1] A. Barla,[1] B. Salce,[1] G. Lapertot,[1] I. Sheikin,[3] K. Matsubayashi,[4] N. K. Sato,[4] and J. Flouquet[1]
[1]*Département de Recherche Fondamentale sur la Matière Condensée, CEA, 38054 Grenoble Cedex 9, France*
[2]*Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan*
[3]*Grenoble High Magnetic Field Laboratory, MPI-FKF/CNRS, Boîte Postale 166 38042 Grenoble Cedex 9, France*
[4]*Department of Physics, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan*
(Received 30 August 2004; published 17 December 2004)

Electrical resistivity and specific heat of SmS in its gold phase have been investigated. Above $P_\Delta = 2$ GPa, the resistivity is characteristic of a metallic heavy fermion compound. Ac calorimetry points out a phase transition with the occurrence of a new ground state. Analyses of the resistivity and of the specific heat and comparison with a microscopic probe (^{149}Sm nuclear forward scattering) allow us to identify the onset of antiferromagnetism. Discussion will be made on the interplay of gap closing ($P < P_\Delta$), long-range magnetism ($P > P_\Delta$), and valence state.

DOI: 10.1103/PhysRevB.70.220406 PACS number(s): 75.30.Kz, 75.30.Mb, 71.27.+a, 81.40.Vw

SmS is a key material to clarify the physics of strongly correlated electronic systems as the valence of Sm is directly coupled to the release of a light $5d$ itinerant electron: $Sm^{2+} \rightleftharpoons Sm^{3+} + 5d$. At zero pressure, the Sm ions are in a divalent insulating state, the so-called black phase. At very high pressure (P), the Sm will be in a trivalent metallic state. Between the two limits, the valence (v) of Sm is intermediate. This transition occurs discontinuously from 2+ to an intermediate valence (IV) value at the well known black-to-gold-phase transition that corresponds to a first-order line $P_{B\text{-}G}(T)$ extensively studied three decades ago.[1–3] At room temperature, $P_{B\text{-}G} = 0.65$ GPa. At low temperature, the first-order transition is accompanied by a large hysteresis; $P_{B\text{-}G}$ ranging between 1.4 down to 0.5 GPa.

In the gold phase $(P > P_{B\text{-}G})$, the change of the valence seems to occur continuously. Previous L_{III} absorption spectra of Sm in SmS (Ref. 4) as well as recent experiments at the European Synchrotron Radiation Facility[5] show that the valence starts with $v = 2.6$ at $P_{B\text{-}G}$, goes through a maximum $\partial v / \partial P$ of its pressure derivative for $P \sim P_\Delta = 2$ GPa with $v = 2.7$, and then smoothly increases. The trivalent state may be reached continuously at $P_{3+} > 10$ GPa. Near 2 GPa, Keller *et al.*[6] have already pointed out an abnormally large pressure derivative of the bulk modulus. Whatever is the pressure by respect to $P_{B\text{-}G}$, the cubic rock-salt structure is preserved. Phonon anomalies through the valence transition have been reported in an inelastic x-ray scattering study.[7] Between $P_{B\text{-}G}$ and $P_\Delta = 2$ GPa, all resistivity measurements[8–11] agree that the system ends up in an insulating phase at low temperature as observed for the other IV systems, such as TmSe, SmB_6, or YbB_{12}.[1] The magnetic susceptibility in this low-pressure gold phase does not show a Curie-Weiss divergence at low temperature. The IV state is a homogeneous nonmagnetic electronic state.[3] Above $P_\Delta = 2$ GPa, again all resistivity experiments indicate a metallic ground state. The resistivity increases on cooling before reaching a maximum at T_M and then decreases. Another phase transition may occur below T_M. When the Sm ion will reach its trivalent state above P_{3+}, a long-range magnetic ordering at T_N must occur since Sm^{3+} is a Kramer's ion with a $2J+1 = 6$ degeneracy (the same angular momentum $J = 5/2$ as Ce^{3+}) and may be lifted into a Γ_7 doublet and a Γ_8 quartet by the cubic crystal field. Thus, when P increases towards P_{3+}, long-range magnetism will appear above a critical pressure P_c as discovered for the ytterbium heavy fermion compounds,[12] the hole analog of the cerium ones. The key questions are first, the localization of P_c with respect to $P_{B\text{-}G}$, P_Δ, and P_{3+}, then the nature of the phase transition (first or second order), and finally, the origin of the ordered moments knowing that different channels are possible with the Sm^{2+} and Sm^{3+} configurations.

At low temperature, the selection of the wave function among those of the $Sm^{2+}(J=0)$ and $Sm^{3+}(J=5/2)$ configuration is the result of a subtle balance. For the well-known IV case of TmSe at $P=0$, the degeneracy of the paramagnetic ground state[13] seems to be that of the doublet of the $Tm^{2+}(J=7/2)$ configuration, despite the fact that the valence is near 2.7–2.8.[1,14] Only above $P = 3$ GPa, does the wave function seem to be that of a trivalent state.[15]

Single crystals of different origins were investigated. All the materials were grown by the Bridgman technique. They were taken from growths realized at Yorktown Height[8,9] in Grenoble and Sendai.[11] As no significant differences were found in the electric and calorimetric behavior, we will not refer later to the sample origin. Piston-cylinder pressure cells were used for resistivity measurements up to 2.4 GPa at low temperature. Transverse magnetoresistance under pressure was measured at the Grenoble High Magnetic Field Laboratory up to 23 T. Specific heat was measured by an ac-calorimetry method in a diamond anvil cell (DAC) using argon as transmitting medium.[16] The sample is thermally linked with a heat bath and heated up by a heater whose power is modulated by a frequency ω. As a result the temperature of the sample oscillates with the same frequency. Assuming that the leakage of heat from the sample to the environment is characterized by a thermal conductivity κ, the amplitude of the temperature oscillation T_{ac} is written as a function of the specific heat C_{ac} of the sample $T_{ac} = Q/(\kappa + i\omega C_{ac})$, where Q is an average of the power transmitted from the heater to the sample. Here it is also assumed that the thermal relaxation within the sample is faster than $1/\omega$. A

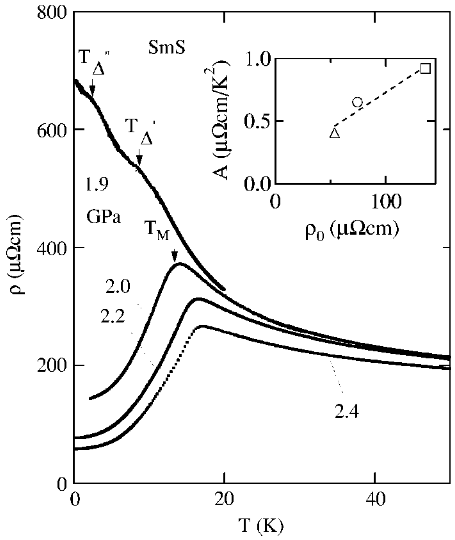

FIG. 1. Temperature dependence of electrical resistivity in gold-phase SmS under pressure. The quadratic coefficient A is plotted against residual resistivity ρ_0 in the inset, for 2 (□), 2.2 (○), and 2.4 (△) GPa.

mechanically chopped laser light was used as a heater. The temperature difference between the sample and the heat bath was measured using a AuFe-Au thermocouple directly bonded on the sample. Frequency around 800 Hz was appropriate to cover the temperature range between 2 and 30 K.

Figure 1 shows the temperature dependence of the resistivity $\rho(T)$ under several pressures above the black-gold transition. Above $P_{\text{B-G}}$, the resistivity at room temperature (around 200 $\mu\Omega$ cm) is one order of magnitude smaller than that in the black phase and is almost the same as that of metallic Sm-based compounds. In agreement with previous data,[8–11] the $\rho(T)$ behavior up to 1.9 GPa is nonmetallic, i.e., the resistivity increases with decreasing temperature. For example for $P=1.9$ GPa, two broad anomalies are seen at around $T_{\Delta''}=2$ K and $T_{\Delta'}=10$ K. Similar features were also found in Refs. 9 and 10, where both $T_{\Delta''}$ and $T_{\Delta'}$ seem to collapse near $P_\Delta=2$ GPa. At 2 GPa, the low temperature variation of $\rho(T)$ is characteristic of a heavy fermion compound (HFC) with a metallic conduction on cooling below a maximum of $\rho(T)$ at T_{M}. With increasing pressure, the position of this peak shifts toward higher temperatures.[8–11,17]

We note that the T^2 behavior of the resistivity is found from 50 mK to 4 K. The quadratic coefficient A estimated for 2 GPa is 0.9 $\mu\Omega$ cm/K^2. If we assume a Kadowaki-Woods relation,[18] it corresponds to a heavy electronic state with a Sommerfeld coefficient $\gamma\sim 300$ mJ/K^2 mol. However, as shown in the inset of Fig. 1, the P dependence of A is strongly correlated with that of the residual resistivity ρ_0. For a given residual mean free path, that points out a change in the carrier concentration. Indeed, a large P dependence of the Hall coefficient R_{H} at 4.2 K has been reported with a change from a large positive value below P_Δ to a small negative contribution slightly above P_Δ. These two concomitant features are a direct evidence of a large increase in electronic carrier density.[17,19]

As the temperature increases above 4 K, the exponent α of the temperature term $A_\alpha T^\alpha$ of $\rho(T)$ increases, this extra

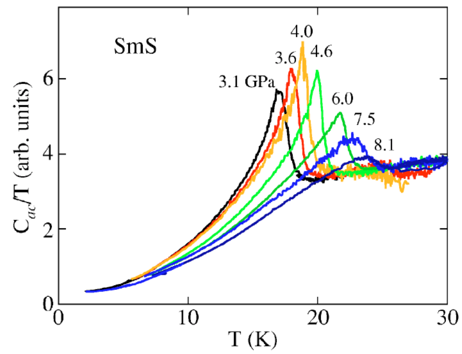

FIG. 2. (Color online) Typical specific heat curves drawn by the temperature variation of C_{ac}/T for several pressures. The data are normalized at 30 K.

contribution is attributed to the spin wave scattering. In the paramagnetic state of HFC, the Fermi liquid term T^2 is found only below a very low temperature regime. Above this temperature regime, the electronic contribution T^α to the resistivity yields always an exponent α lower than two for nonmagnetically ordered HFC. A value of α greater than two is found for AF ground states even close to P_c.[20] The observation of a positive departure from $\rho=\rho_0+AT^2$ law is a first signature that T_{M} may be related to the Néel temperature (T_{N}) of an antiferromagnetic ground state. We have, of course, checked if superconductivity appears near the critical pressure P_Δ by performing resistivity measurements down to 50 mK; at least in the present stage of the sample quality no superconductivity has been detected.

Transverse magnetoresistance up to $H=23$ T at 2.4 GPa has been measured. The magnetoresistance is always very small. This weak H sensitivity has been confirmed for other pressures up to 7 T. It contrasts with the huge negative magnetoresistance observed in the black phase.[21] Let us remark that the Sm-based cubic antiferromagnet SmSb appears weakly sensitive to a magnetic field of 10 T.[22] Having reconfirmed that the appearance of the resistive anomaly T_{M} is sample independent, we show specific heat measurements under high pressure.

Figure 2 shows the result of ac-calorimetric study under high pressures up to 8.1 GPa. The specific heat C has been derived from the amplitude of the temperature oscillation. Because we do not know the exact power transmitted to the sample from the laser light, we could not obtain the absolute value of the specific heat. The specific heat value has been normalized at 30 K, which is sufficiently higher than the transition temperature. At 3.1 GPa, a prominent anomaly is seen at $T_{\text{N}}=17$ K. This result shows directly the presence of a phase transition in the gold phase of SmS. In parallel to these calorimetric experiments, hyperfine interaction measurements on Sm nuclei using the nuclear forward scattering (NFS) technique show that, just above P_Δ, a hyperfine field H_{hf} as well as a quadrupolar splitting appear below a temperature $T_{\text{NFS}}>T_{\text{N}}$.[23] Furthermore from both hyperfine signatures, the samarium state appears to be that of the Γ_8 quartet of Sm^{3+}. As $T_{\text{NFS}}>T_{\text{M}}>T_{\text{N}}$, slow spin dynamics (electronic relaxation time is greater than 10^{-10} s) appears already far above T_{N} (Fig. 3).

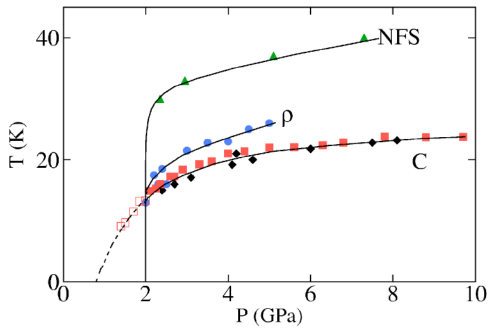

FIG. 3. (Color online) Pressure dependence variation of T_{NFS} (▲), T_M (●), and T_N (■ and ◆) detected in NFS, resistivity (ρ) and two independent calorimetric experiments (C). Continuous lines have been drawn for eyes above P_Δ. Below P_Δ, the temperature of the maximum of C has also been reported (□).

To see the evolution of the phase transition around P_Δ, the sharpness $T_N/\Delta T_N$ of the specific anomaly through P_Δ is compared in Fig. 4 with the fraction f of magnetic sites detected by NFS (ΔT_N was chosen by the temperature window where the specific heat anomaly reaches half of its maximum). The simultaneous step increase of $y=T_N/\Delta T_N$ and f at $P_c=P_\Delta$, demonstrates a drastic change from a paramagnetic short-range-ordered (SRO) phase and a long-range-ordered (LRO) phase. This statement is reinforced by the fast increase of the calorimetric signal through P_Δ. From 2 up to 4 GPa, the pressure variation of T_N is large: 15 K at P_Δ, to 21 K at 4 GPa. Above 4 GPa, the pressure dependence of T_N is smaller : $T_N=24$ K at 8 GPa. The values of T_{NFS} are 30 K for $P=2.35$ GPa and 45 K for $P=10$ GPa. Roughly T_{NFS} and T_N differ by a factor near two. The broadening of the calorimetric signal at high pressure ($P>5$ GPa) appears to be an experimental artifact due to an attenuation of the thermocouple voltage. Experiments on the highly documented system TmSe up to 13 GPa have shown that the position of the ordering temperature is well defined and in excellent agreement with published works, but the amplitude of the thermocouple signal is strongly reduced at high pressure.[24]

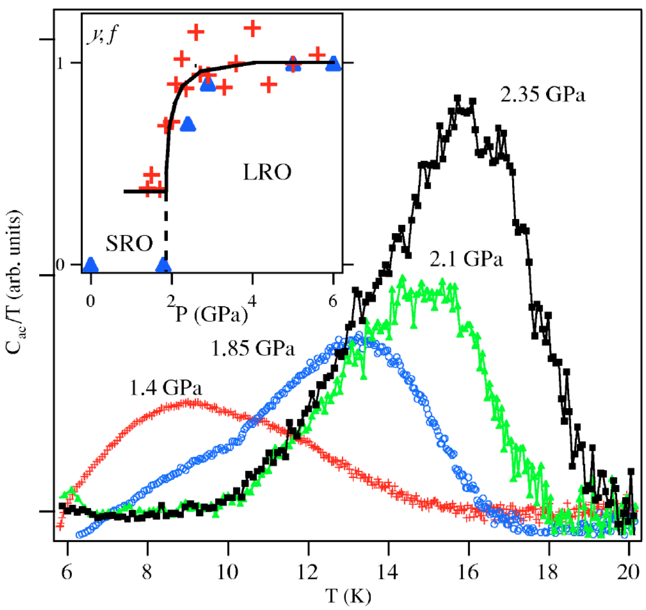

FIG. 4. (Color online) Zoom of the specific heat near P_Δ, in arbitrary units. The inset shows the normalized sharpness (+) of the specific heat anomaly defined by $y=T_N/\Delta T_N$ and the magnetic fraction f found by NFS (▲).

Although our ac calorimetry in a DAC is semiquantitative, it appears that the specific heat behaves roughly as $C_{ac}=\gamma T+\beta T^3$. An antiferromagnetic ground state explains well the second term, i.e., a spin-wave spectrum with vanishing energy gap. By assuming that the entropy variation at T_N corresponds to a Γ_8 quartet ground state, a mean value of 180 mJ/K^2 mol is estimated. The occurrence of a heavy fermion behavior is confirmed. The invariance of C/T at $T\to 0$ K is characteristic of a magnetically ordered HFC far from P_c with a strong interplay between Kondo energy and exchange interaction.[25]

The striking point is that a similar γ value was also found in the low pressure gold phase below P_Δ.[26,27] From the broadened calorimetric feature below P_Δ, strong magnetic correlations coexist obviously with the localization of the charge of the 5d electron involved in the balance of the two Sm^{2+} and Sm^{3+} states. Evidence of SRO exists in NFS experiments:[28] the NFS spectra for $1.6<P<2$ GPa at low temperature ($T\sim 2$ K) can only be fitted with a broad distribution of hyperfine parameters. The previous $T_{\Delta'}$ signature in the ρ measurements was already associated to a possible onset of magnetic correlations.[11] The collapse of the broadened SRO's feature occurs for $P\sim 1.3$ GPa, i.e., near the pressure of the B–G transition. Let us stress that by the analysis of the electron spin resonance ESR and susceptibility measurements, a rather large ferromagnetic exchange coupling (11 K) was found in the black phase of SmS;[29] the magnetic ordering is precluded by the weakness of the mixing between the $J=0$ and $J=1$ configuration of Sm^{2+}.

Obviously slow magnetic fluctuations appear far above T_N for $P>P_\Delta$. The precession of local moments around the nuclei is observed for a pressure far below P_{3+}. Such a phenomenon has been reported recently in ESR experiments of $YbRh_2Si_2$, despite the relatively large value given for its Kondo temperature ($T_K=25$ K).[30] The divalent memory of the Tm ions in TmSe, almost up to the entrance in the trivalent phase, has been already noticed. Furthermore, as for the low-pressure gold phase of SmS, TmSe is an insulator up to 3 GPa. In both cases, the normalization to the divalent or trivalent configuration is coupled to the mode of the electric conduction reminiscent of the pure 2+ state (insulator) or of the pure 3+ state (metallic). A change in the localization of the 5d electrons leads to a switch in the microscopic nature of the magnetism (spatial shape of the 4f wave function) as well as in its long-range appearance.

The present interplay between localization of the carrier, valence, and magnetism must push also to unravel the nature of the so-called magnetic quantum critical point and the related possible Fermi surface instabilities in HFC. For the cerium cases as $CeRh_2Si_2$, there is already evidence of magnetic quantum first-order transitions near P_C associated with drastic modifications of the Fermi surface,[31] the competition between the Kondo energy, and the crystal field splitting explains well the microscopic nature of the magnetism. Similar considerations for the fluctuations between $4f$ configurations of different valence states are clearly required.

To summarize, at $P_{\Delta} \ll P_{3+} \sim 10$ GPa, the entrance in the metallic IV phase is coupled to the onset of long range magnetism ($P_{\Delta} = P_c$) and to the switch to the renormalization of the wavefunction to the Sm^3+ configuration. The insulating low-pressure gold phase of Sm is a "sloppy" insulating matter with short-range magnetic correlations.

Experimental developments on $C_{ac}(T,P)$ were supported by "Region Rhône-Alpes / France" through the "Emergence" Grant No. 00 81 60 87/88.

[1] See P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, L. Eyring, G. H. Lander, and G. R. Choppin (Elsevier Science B.V., Amsterdam 1994), Vol. 19, p. 177.

[2] A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. **25**, 1430 (1970).

[3] M. B. Maple and D. Wohlleben, Phys. Rev. Lett. **27**, 511 (1971).

[4] J. Röehler, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10, p. 453.

[5] C. Dallera *et al.*, J. Phys.: Condens. Matter (to be published).

[6] R. Keller, G. Güntherodt, W. B. Holzapfel, M. Dietrich, and F. Holtzberg, Solid State Commun. **29**, 753 (1979).

[7] S. Raymond, J. P. Rueff, M. D'Astuto, D. Braithwaite, M. Krisch, and J. Flouquet, Phys. Rev. B **66**, 220301(R) (2002).

[8] F. Holtzberg and J. Wittig, Solid State Commun. **40**, 315 (1981).

[9] F. Lapierre, M. Ribault, F. Holtzberg, and J. Flouquet, Solid State Commun. **40**, 347 (1981).

[10] M. Konczykowski, J. Morillo, and J. P. Senateur, Solid State Commun. **40**, 517 (1981).

[11] M. Ohashi, D. Kondo, N. Sato, T. Suzuki, T. Komatsubara, H. Takahashi, and N. Môri, Rev. High Pressure Sci. Technol. **7**, 611 (1998).

[12] J. Plessel, M. M. Abd-Elmeguid, J. P. Sanchez, G. Knebel, C. Geibel, O. Trovarelli, and F. Steglich, Phys. Rev. B **67**, 180403(R) (2003).

[13] A. Berton, J. Chaussy, B. Cornut, J. Flouquet, J. Odin, J. Peyrard, and F. Holtzberg, Phys. Rev. B **23**, 3504 (1981).

[14] G. Kaindl, G. Kalkowski, W. D. Brewer, E. V. Sampathkumaran, F. Holtzberg, and A. Schach v. Wittenau, J. Magn. Magn. Mater. **47-48**, 181 (1985).

[15] M. Ribault, J. Flouquet, P. Haen, F. Lapierre, J. M. Mignot, and F. Holtzberg, Phys. Rev. Lett. **45**, 1295 (1980).

[16] B. Salce, J. Thomasson, A. Demuer, J. J. Blanchard, J. M. Martinod, L. Devoille, and A. Guillaume, Rev. Sci. Instrum. **71**, 2461 (2000).

[17] M. Konczykowski, F. Lapierre, P. Haen, J. Morillo, and J. P. Sénateur, J. Magn. Magn. Mater. **47-48**, 274 (1985).

[18] K. Kadowaki and S. B. Woods, Solid State Commun. **58**, 307 (1986).

[19] N. Mori, T. Nakanishi, M. Ohashi, N. Takeshita, H. Goto, S. Yomo, and Y. Okayama, Physica B **265**, 263 (1999).

[20] A. Demuer, I. Sheikin, D. Braithwaite, B. Fåk, A. Huxley, S. Raymond, and J. Flouquet, J. Magn. Magn. Mater. **226-230**, 17 (2001).

[21] M. Konczykowski, P. Haen, J. C. Portal, and J. P. Sénateur, J. Magn. Magn. Mater. **47-48**, 455 (1985).

[22] S. Ozeki, Y. S. Kwon, Y. Haga, T. Suzuki, G. Kido, and T. Kasuya, Physica B **169**, 499 (1991).

[23] A. Barla, J. P. Sanchez, Y. Haga, G. Lapertot, B. P. Doyle, O. Leupold, R. Rüffer, M. M. Abd-Elmeguid, R. Lengsdorf, and J. Flouquet, Phys. Rev. Lett. **92**, 066401 (2004).

[24] J. Derr *et al.* (unpublished).

[25] J. Flouquet, P. Haen, P. Lejay, P. Morin, D. Jaccard, J. Schweizer, C. Vettier, R. A. Fisher, and N. E. Phillips, J. Magn. Magn. Mater. **90-91**, 377 (1990).

[26] S. D. Bader, N. E. Phillips, and D. B. McWhan, Phys. Rev. B **7**, 4686 (1973).

[27] K. Matsubayashi, H. Mukai, T. Tsuzuki, T. Nishioka, and N. K. Sato, Physica B **329-333**, 484 (2003).

[28] A. Barla, J. P. Sanchez, J. Derr, B. Salce, G. Lapertot, J. Flouquet, B. P. Doyle, O. Leupold, R. Rüffer, M. M. Abd-Elmeguid, and R. Lengsdorf, J. Phys.: Condens. Matter (to be published).

[29] R. J. Birgeneau, E. Bucher, L. W. Rupp, Jr., and W. M. Walsh, Jr., Phys. Rev. B **5**, 3412 (1972).

[30] J. Sichelschmidt, V. A. Ivanshin, J. Ferstl, C. Geibel, and F. Steglich, Phys. Rev. Lett. **91**, 156401 (2003).

[31] S. Araki, R. Settai, T. C. Kobayashi, H. Harima, and Y. Ōnuki, Phys. Rev. B **64**, 224417 (2002).