Elastic anomalies associated with possible charge order and other transitions in mixed-valent YbPd

Y. Nakanishi,[1,*] T. Kamiyama,[1] K. Ito,[1] M. Nakamura,[1]
M. Sugishima,[2] A. Mitsuda,[2] H. Wada,[2] and M. Yoshizawa[1]

[1]*Graduate School of Engineering, Iwate University, Morioka, Japan*
[2]*Department of Physics, Kyushu University, Fukuoka, Japan*
(Received April 6, 2010)

Elastic anomalies associated with possible charge order and other phase transitions in a mixed-valent compound YbPd were investigated by ultrasonic measurements. A pronounced elastic anomaly was observed at a possible charge-ordering temperature of 125 K, accompanied with a distinct hysteresis. On the other hand, a slight but clear elastic anomaly was observed at other phase transitions at 1.9 K and 105 K. We argue that the data can be described in terms of $4f$ low-lying level scheme of Yb ions under a crystalline electric field effect and a possible charge ordering although Yb seems to go into a mixed-valent state in YbPd.

I. INTRODUCTION

In recent years, much attention has been focused on Yb compounds due to a rich variety of physical phenomena derived from a mixed-valent state of Yb ion, such as magnetism, multipolar ordering, charge ordering, heavy fermion (HF) behavior, non-fermi liquid behavior and superconductivity. In particular, the mixed-valent state of Yb ions is of central importance in these systems.[1–3] The magnetic properties of compounds with such unstable f shells are particularly interesting because of the potential competition between the hybridization of the f electron with the conduction band, which tends to dissolve the crystalline electric field (CEF) fashioned f-shell moment, and the exchange interactions, which can act to stabilize these moments. The key point here is that Yb ions fluctuate between the nonmagnetic Yb^{2+} ($J = 0$) and the magnetic Yb^{3+} ($J = 7/2$) states. Thus, magnetic order or/and multipolar ordering of Yb ions is quite unexpected in metals to date.

The cubic CsCl-type compound YbPd is one of such rare metals in the Yb-based compounds. It undergoes four phase transitions at 0.5 K, 1.9 K, 105 K, and 125 K determined by specific heat, thermal expansion, and electrical resistivity measurements.[4] Furthermore, a comprehensive experimental study was also made using different microscopic techniques. From magnetic susceptibility measurements, the transition at 0.5 K is found to be magnetic. The ^{170}Yb Mössbauer effect measurements suggest that another magnetic ordering occurs at 1.9 K, and the saturated spontaneous magnetic moment is 1.15 μ_B, which is lower than that in any of the Yb^{3+} cubic crystalline electric levels.[5] These facts turn out that YbPd is a very interesting system since the magnetic ordering

occurs clearly at fractional valence, being near configurational crossover of $4f^{13}$ and $4f^{14}$. It suggests that $4f$–conduction-band hybridization would be present and play an important role in this system. YbPd is, in fact, found to be a homogeneous mixed-valence compound with the valence changing from 2.82 at 300 K to 2.80 near $T = 0$, confirmed by L_{III} x-ray measurements. [4]

On the other hand, distinct inelastic excitations were observed by inelastic magnetic neutron scattering measurements on YbPd.[6] These spectra can be interpreted in terms of CEF theory for trivalent Yb in cubic symmetry. Hund's rule ground multiplet of $4f^{13}$ configuration is as follows: Yb^{3+} is $J = 7/2$, which splits into Γ_8 quartet, Γ_7 doublet, and Γ_8 doublet under the cubic CEF. They propose the corresponding CEF level scheme of Γ_8(0 K) – Γ_7(55 K) – Γ_6(142 K). It seems surprising to have such a small total splitting less than 55 K, which is approximately the same magnitude of the highest transition temperature of 125 K. This fact also suggests that the four phase transitions in YbPd would possibly involve the all $4f$ states, Γ_8 quartet, Γ_7 doublet, and Γ_6 doublet. It should be mentioned here that the unequivocal existence of two inelastic excitations suggests a $4f$ well-localized character of Yb^{3+}, which is totally inconsistent with mixed-valent argument of Yb ions above. It still remains a tough enigma.

YbPd exhibits other two phase transitions at 105 K and 125 K, which can be observed as strong anomalies in the specific heat and the thermal expansion data.[4] These mechanisms have not been fully understood at present. Initially, these transitions were considered to be structural, although this could not be confirmed. The ^{170}Yb Mössbauer effect measurements also suggest that two different Yb charge states are present in equal proportions at the lowest temperature, which implies charge ordering, although Yb ion occupies only one crystallographic site in the CsCl-type structure.[5] Thus, one of the transitions seems to be charge ordering. Another feature is that YbPd shows an enhanced Sommerfeld coefficient of the specific heat γ exceeding 600 mJ/mol K^2, indicating HF behavior. If the ground-state properties in this compound are governed by the competition between the RKKY interaction and the Kondo interaction, the system is located near a valence and resultant magnetic instability. Thus, it seems that YbPd is an interesting system due to its proximity to a magnetic quantum critical point (QCP) in this sense.

In this way, although extensive studies on YbPd compound has been done and revealed unusual properties attributed to the mixed-valent state of Yb ions, the situation is far from reaching a consensus on complete understanding.

In this study, we performed ultrasonic measurements on a polycrystalline sample of the mixed-valent compound YbPd to investigate the elastic property in the vicinity of the phase transition temperatures. A pronounced elastic anomaly was observed in the temperature dependence of longitudinal and transverse modes at the possible charge-ordering temperature of 125 K, being accompanied with a clear hysteresis. On the other hand, a slight but clear elastic anomaly was observed in the temperature dependence of longitudinal and transverse modes at other phase transitions at 1.9 K and 105 K. Since no single crystals are available to date for this compound, we show and discuss only the experimentally accessible modes, i.e., C_L and C_T.

II. EXPERIMENTAL

Polycrystalline sample of YbPd was prepared by an ingot of ytterbium metal with the purity of 99.9 % and 99.95 % as a starting material.[7] The mixture of shavings of the Yb metal and the Pd powder in a ratio of 1.3:1 was pressed into a pellet. The pellet, which was sealed into a tantalum tube under argon atmosphere by using an arc-furnace, was heated at 1450 °C for 40 h. Powder x-ray diffraction pattern shows that the sample is in the cubic CsCl-type structure with a lattice constant of a = 3.439 Å. The sample used in our study has a size of $2.1 \times 1.9 \times 2.2$ mm^3.

The sound velocity, as the elastic constant was measured by an ultrasonic apparatus based on a phase-comparison method at temperatures down to 0.5 K in magnetic field up to 12 T. Plates of LiNbO$_3$ was used as the piezoelectric transducer. The fundamental resonance frequency of LiNbO$_3$ transducer is 5–30 MHz. The transducer was glued on the parallel planes of the sample by an elastic polymer Thiokol. The absolute value of the sound velocity was obtained by measuring the delay time between the ultrasonic echo signals with an accuracy of a few percent. The elastic constant was calculated as $C = $ g$\rho v^2$by using the sound velocity $v$and the density ρ of the crystal. The lattice constant of YbPd at room temperature a = 3.439 Å was used for the estimation of the density $\rho = 11.41$ g/cm^3.

III. EXPERIMENTAL RESULTS

We measured the longitudinal as well as transverse ultrasonic velocity. We used 10–30 MHz for the measurement of C_L and 5–15 MHz for C_T. Figure 1 shows the temperature (T) dependence of longitudinal and transverse modes measured on the polycrystalline YbPd sample. The absolute values of elastic constants and calculated Lamé's constants λ and μ at both 77 K and 4.2 K are listed in Table I. Lamé's constants λ and μ are described by C_L and C_T as $C_L = \lambda + 2\mu$ and $C_T = \mu$. Thus, bulk modulus K, Young's modulus Y, and Poisson's ratio σ are calculated by $K = \lambda + 2\mu$vzs $Y = \mu (3\lambda + y\mu)/(\lambda +g\mu)$, and $\sigma = \lambda$vy$(\lambda +$g$\mu)$, respectively. There are several anomalies at around the phase transition temperatures of 1.9 K, 105 K, and 125 K. A pronounced elastic softening was observed in C_L and C_T at a critical temperature of 125 K. The ultrasonic signal becomes so small and unstable at around 125 K that it is so hard to measure the complete change in the sound velocity that takes place at the phase transition. This behavior is typical for the discontinuous phase transition such as a charge ordering, valence phase transition.[8–10] The elastic constants C_L and C_T change about 14% and 10%, respectively, at the phase transition temperature of 125 K. It is noted that a rather slight anomaly was observed at the critical temperature of 105 K in both C_L and C_T, which is much smaller than that observed at around 125 K. The softening for C_L and $C_T$amounts to 0.4% and 0.6%, respectively. On the other hand, a sudden elastic hardening was observed below 1.9 K in both C_L and C_T. This behavior is typical for a magnetic phase transition.

Figure 2 shows the temperature dependence of longitudinal and transverse modes measured on the polycrystalline YbPd sample under the selected magnetic fields, which are
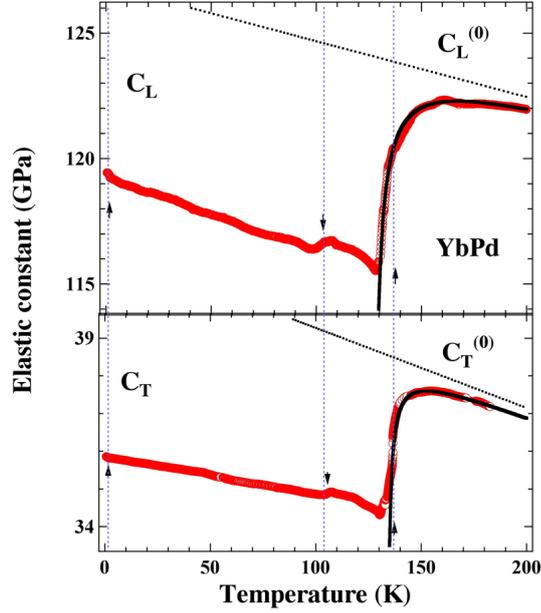
FIG. 1: The temperature dependence of elastic constants C_L and C_T of YbPd. The solid lines denote the calculated curves based on the formula (3) in text. The dotted lines are the background elastic constants C_Γ^0 for fitting. The arrows and vertical dotted lines indicate the transition temperature points.

TABLE I: The absolute values of longitudinal elastic constants C_L, transverse one C_T, Lamé's constants λ, bulk modulus K, Young's modulus Y, and Poisson's ratio σ at both 77 K and 4.2 K.

	C_L (GPa)	$C_T = \mu$ (GPa)	λ (GPa)	K (GPa)	Y (GPa)	σ
4.2 K	119.15	35.81	47.53	71.40	92.04	0.285
77 K	116.94	35.09	46.76	70.15	90.23	0.286

offset for clarity in ascending order from bottom to top. There are several features seen in the field dependence of the elastic constants as a function of temperature. First, the abrupt decrease in elastic constantC_L and C_T shifts hardly, but slightly to lower temperatures and then the decrease becomes suppressed slightly by applying the magnetic field. Here, red and blue lines denote the results on heating and cooling, respectively. It should be noted that a distinct hysteresis is observed under the magnetic field, which indicates a first-order phase transition that will be discussed in detail below. The slight anomaly observed C_L–T and C_T–T around 105 K in zero field becomes suddenly obscure, implying that the origin might be magnetic.

On the other hand, the sudden elastic hardening observed below 1.9 K in both C_L–T and C_T–T shifts significantly to lower temperatures and the hardening becomes gradually
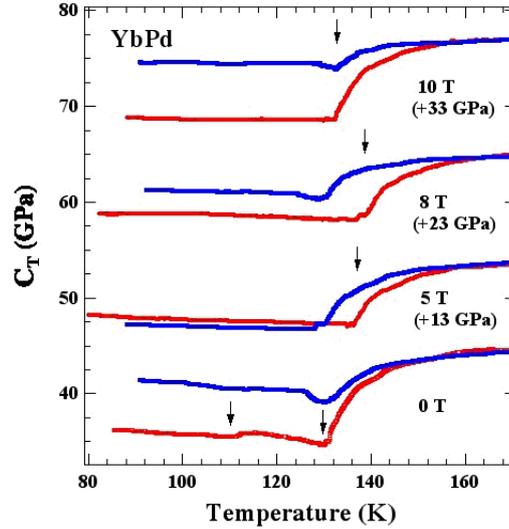
FIG. 2: The temperature dependence of the transverse mode measured on the polycrystalline YbPd sample under the selected magnetic fields. Here, red and blue lines denote the results on heating and cooling, respectively. The arrows indicate the transition temperature points.

depressed on applying the magnetic field as shown in Fig. 3. Above 3 T, the anomaly is undetectable, indicating that the ground state has a magnetic character.

From these experimental results, the magnetic (H–T) phase diagram of YbPd was deduced as shown in Fig. 4. The boundary of the low-temperature phase indicated by the closed black circles goes up to the higher field side with a negative curvature and closes completely around 2.8 T. Again, this behavior is typical for a magnetic phase transition, being in consistent with prediction by the ^{170}Yb Mössbauer effect measurements.[5]

IV. DISCUSSION

First, let us discuss elastic anomalies showing up around 125 K. The pronounced elastic softening toward the transition temperature of 125 K, as observed in C_L–T and C_T–T can be approached by different theories, depending on the origin. We will analyze this elastic anomaly by the two following scenarios: 1) CEF effect and 2) charge ordering. However, we can show the only experimentally accessible analysis 2) since no single crystals are available for YbPd in the c present study. It should be noted here that we do not rule out scenario 1). According to the proposed CEF level scheme, the ground state of Yb^{3+} ($4f^{13}$) is the well-isolated Γ_8 quartet in YbPd.[6] Thus, one would expect typical quadrupolar effects in C_L–T and C_T–T for $T > 125$ K since the Γ_8 quartet ground state of the Yb^{3+} ions is both of Γ_3 and Γ_5 quadrupolar – active. Scenario 1) will be discussed in detail in a separated article soon after the same measurements on single crystals are completed.[11]
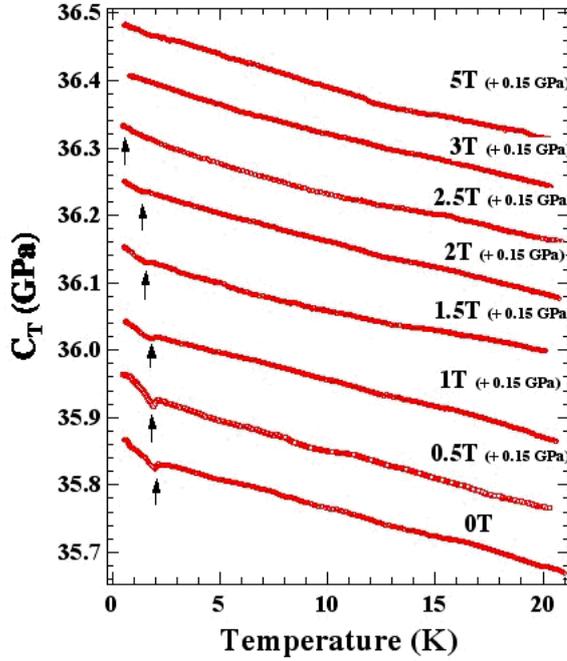
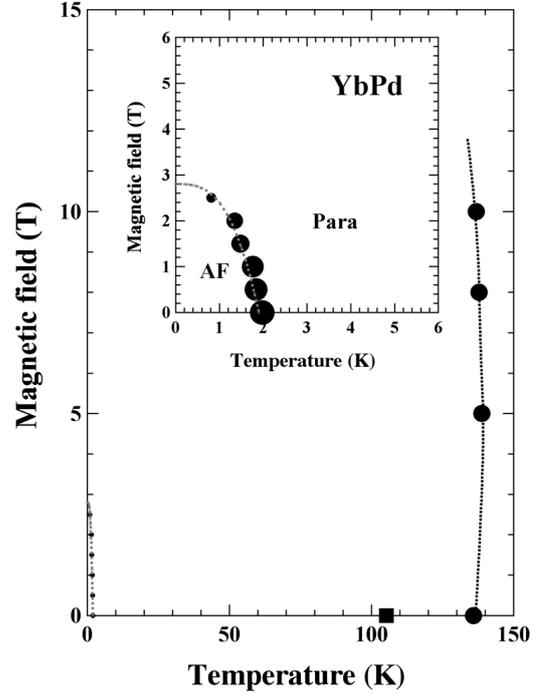FIG. 3: Low temperature part of the elastic constant C_T of YbPd. The arrows indicate the transition temperature points.

FIG. 4: Magnetic (H–T) phase diagram of YbPd as deduced from the present results. The dotted lines are a guide to the eyes. Inset shows the low temperature part of the phase diagram.

The elastic softening of a localized f electrons system is usually understood as the quadrupolar response of the system to an external strain associated with a sound wave. A detailed derivation should be referred somewhere.[12–16] The temperature dependence of the symmetric elastic constant C_Γ is finally described as

$$C_\Gamma = C_\Gamma^0 - \frac{N g_\Gamma^2 \chi_\Gamma^s}{1 - g_\Gamma' \chi_\Gamma^s} \tag{1}$$

Here, N denotes the number of Yb ions in unit volume, C_Γ^0 the background elastic constant, χ_Γ^s the corresponding strain susceptibility, g_Γ the magnetoelastic coupling constant, and $g_\Gamma\prime$ the wave vector $\boldsymbol{q} = 0$ interaction between the quadrupoles in the Hamiltonian

$$H = -\sum_i g_\Gamma \varepsilon_\Gamma O_{\Gamma i} - \sum_i g_\Gamma' \langle O_\Gamma \rangle O_{\Gamma i}, \tag{2}$$

where ε_Γ denotes the symmetry strain and O_Γ is the corresponding quadrupolar operator. Details should be referred somewhere. If one replace the quadrupolar operator O_Γ with another order parameter Q_Γ, which can be due to the charge fluctuation mode characterized

by the wave vector $\boldsymbol{q} = 0$ at the Brillouin zone center Γ point, then the above formula (1) can be rewritten as follows:

$$C_\Gamma = C_\Gamma^0 \left(\frac{T - T_Q}{T - \Theta} \right), \tag{3}$$

where C_Γ^0 is the background elastic constant, T_Q a critical temperature, and Θ the paramagnetic Curie-Weiss constant. This formula is used for the cooperative Jahn-Teller effect.[10] The critical temperature T_Q corresponds to the elastic instability point for the second-order transition represented by $T_Q = g\Theta + A$, where A is the coupling energy between the fluctuation mode of order parameter and elastic strains ε_Γ. The fitting curves, as shown in Fig. 1 for C_L–T and C_T–T for $T > 125$ K based on the formula (3), give us important microscopic parameters as follows: $C_L^0 = 126.9 - 0.0223 \times T$ (GPa), $T_Q = 126.2$ K and $\Theta = 125.9$ K for C_L, and $C_T^0 = 41.23 - 0.0212 \times T$ (GPa), $T_Q = 129.6$ K and $\Theta = 129.4$ K for C_T. Here, it should be noted that the paramagnetic Curie-Weiss constant Θ s closely related to the coupling constant between order parameters. If the order parameter is the quadrupolar operator O_Γ s expected by scenario 1), an extremely large quadrupolar interaction would be mediated among quadrupolar moments of Yb^{3+} ions. As a result, one can naturally expect that a quadrupolar ordering will occur at 125 K, which would be the highest transition temperature so far. At present, we cannot conclude this origin whether the transition is due to a quadrupolar ordering or not.

Next let us discuss this transition in terms of other scenario 2). A pronounced elastic softening toward the transition temperature is expected when a charge ordering occurs as seen in Yb_4As_3, Fe_2O_3, for example.[8–10] According to the calculation based on the formula (3), one obtains the coupling energy A as 0.3 K, which corresponds to the coupling constant between the charge fluctuation mode and the elastic strain one. This rather small coupling constant value might lead to the lack of a structural phase transition. Since so far, no structural phase transition neither nor change of valence is observed at around 125 K by the x-ray, thermal expansion, and LIII absorption measurements, doubt about the relevance of charge ordering for the interpretation would raise. However, if the configuration of Yb^{2+} and Yb^{3+} ions is assumed as shown in Fig. 5 in which Yb^{2+} and Yb^{3+} ions occupy alternatively in three-dimensional space, then one can observe no structural phase transition at 125 K. This interpretation can be one candidate.

Finally, we would like to mention the other phase transitions showing up at 1.9 K and 105 K. As mentioned above, the transition at 1.9 K seems to be a magnetic ordering as judged from the magnetic (H–T) phase diagram of YbPd. However, another problem then rises about what happens at 0.5 K where a clear cusp-like anomaly with a clear hysteresis is observed in the magnetic susceptibility. This point is an open problem.

To date, there is no idea regarding the transition showing up at 105 K, although a distinct peak was observed in the specific heat measurement. [4] Since the magnitude of elastic anomaly is much less compared to that of other ones, it seems that neither a structural nor charge phase transition occurs at 105 K. This is still an open question. However, it should be mentioned here that our recent same measurements under pressure indicate a growth of the anomaly originated from the transition showing up at 105 K by
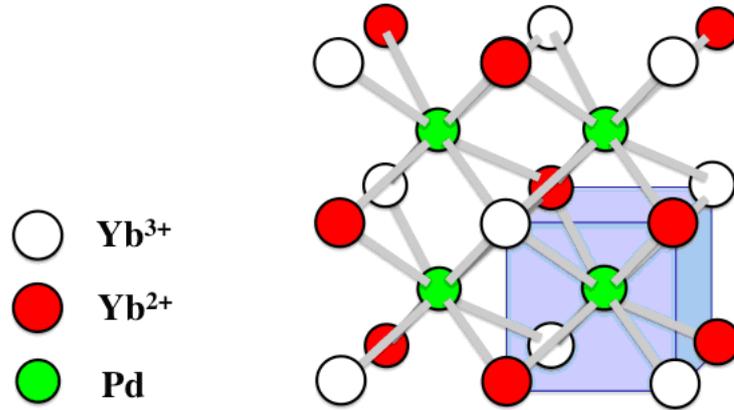
FIG. 5: The possible charge-ordered structure below 125 K in YbPd in which no structural phase transition takes place.

applying the pressure. We will present the pressure dependence of the elastic properties in a separate article soon. [11]

V. CONCLUSIONS

In this paper, we presented the elastic properties of polycrystalline YbPd. We measured the temperature and field dependences of elastic constants C_L and C_T. From these experiments, we obtained the following conclusions. A pronounced elastic softening towards the transition temperature of 125 K was observed in the temperature dependence of C_L and C_T. The magnetic phase diagram of this transition was made, which reveals that the ordering is quite robust against magnetic fields. This means that the phase transition showing up at 125 K would be of a nonmagnetic origin, such as charge ordering or quadrupolar one. A slight elastic anomaly was observed at around 105 K in the temperature dependence of C_L and C_T. This anomaly is much less remarkable than that observed at 125 K although the specific heat data exhibits a clear and sharp peak at 105 K. A clear hardening was observed below 1.9 K in the temperature dependence of C_L and C_T. This behavior makes us reminiscent of antiferromagnetic phase, which is consistent with the previous results. However, how the mixed-valent state of Yb ions in YbPd works as a magnetic or/and quadrupolar ordering mechanism is still an open question. For deeper understanding of the origin of four successive ordering in YbPd, microscopic experiments such as neutron diffraction and nuclear magnetic resonance measurements are highly desired. For further discussion, the same measurements performed under high pressure are currently in progress. In our very recent experiment, the phase transition below 105 K is enhanced and it becomes stabilized on applying pressure. Both the transitions at 105 K and 125 K are largely dependent on the pressure, most probably reflecting on the mixed-valent state of Yb ions in YbPd. Fur-

thermore, in order to elucidate the low temperature phase showing up below 0.5 K, the same measurements are also currently taken by means of a ^{3}He/^{4}He dilution refrigerator, which is cooled down to the temperature of 40 mK. We believe that the present study deserves further investigation to obtain a deeper insight into the mixed-valent state in Yb compounds.

Acknowledgments

References

* Electronic address: `yoshiki@iwate-u.ac.jp`

[1] M. S. Torikachvili, S. Jia, E. D. Mun, S. T. Hannahs, R. C. Black, W. K. Neils, D. Martien, S. L. Bud'ko, and P. C. Canfield, Proc. Nati. Acad. Sci. USA. **104,** 9960-9963 (2007).

[2] M. Kosaka, Y. Kato, C. Araki, N. Mori, Y. Nakanishi, M. Yoshizawa, K. Ohoyama, C. Martin and S. W. Tozer, J. Phys. Soc. Jpn. **74,** 2413-2416 (2005).

[3] S. Nakatsuji, K. Kuga, Y. Machida, T. Tayama, T. Sakakibara, Y. Karaki, H. Ishimoto, S. Yonezawa, Y. Maeno, E. Pearson, G. G. Lonzarich, L. Balicas, H. Lee and Z. Fisk, Nat. Phys. **4,** 603-607 (2008).

[4] R. Pott, W. Boksch, G. Leson, B. Politt, H. Schmidt, A. Freimuth, K. Keulerz, J. Langen, G. Nuemann, F. Oster, J. Röhler, U. Walter, P. Weidner, and D. Wohlleben, Phy. Rev. Lett. **54,** 481-484 (1985).

[5] P. Bonville, J. Hammann, J. A. Hodges, P. Imbert, and G. J. Jéhanno, Phy. Rev. Lett. **57,** 2733-2736 (1986).

[6] U. Walter, and Wohlleben, Phy. Rev. B. **35,** 3576-3584 (1987).

[7] A. Mitsuda, K. Yamada, M. Sugishima, and H. Wada, Physica B. **404,** 3002-3004 (2009).

[8] A. Ochiai, T. Suzuki, T. Kasaya, J. Phys. Soc. Jpn. **59,** 4129 (1990).

[9] E. J. W. Verwey, Nature (London) **144,** 327 (1939).

[10] T. Goto, Y. Nemoto, A. Ochiai and T. Suzuki, Phy. Rev. B. **59,** 269-276 (1999).

[11] Y. Nakanishi (in preparation).

[12] B. Lüthi, J. Magn. Magn. Mater. **52,** 70 (1985).

[13] M. E. Mullen, B. Lüthi, P. S. Wang, E. Bucher, L. D. Longinotti, J. P. Maita, and H. R. Ott, Phys. Rev. B. **10,** 86 (1974).

[14] S. Nakamura, T. Goto, Y. Ishikawa, S. Sakatsume and M. Kasuya, J. Phys. Soc. Jpn. **63,** 623 (1994).

[15] P. Thalmeier, J. Magn. Magn. Mater. **76&77,** 299 (1988).

[16] P. M. Levy, J. Phys. **C. 6,** 3545 (1973).