Metallic ground state of CeNiSn

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(Received 18 March 1998; revised manuscript received 4 September 1998)

The electronic ground state of CeNiSn has been investigated by means of specific-heat measurements below 2 K in magnetic field up to 5 T using a high-quality single crystal. Unusual temperature and field dependence of specific heat reveals that the density of states of CeNiSn has a peak at E_F inside the pseudogap. We claim that CeNiSn is no longer a Kondo insulator but a metal at the lowest temperature. [S0163-1829(99)01204-7]

I. INTRODUCTION

The crystal structure of CeNiSn is of an orthorhombic ϵ-TiNiSi type.[1] Reflecting the crystal structure, the electronic and magnetic properties exhibit strongly anisotropic behavior.[2] When magnetic field is applied along the a axis, which is the easy magnetization axis, significant field effects are observed in various electronic properties. Sommerfeld coefficient γ of specific-heat[3] and spin-lattice relaxation rate $1/T_1$ observed by nuclear magnetic resonance of ^{119}Sn (Ref. 4) suggest a V-shaped pseudogap with a residual density of states (DOS) around the Fermi level E_F. Ikeda and Miyake[5] have theoretically predicted that a residual DOS could intrinsically exist inside the pseudogap. The specific heat[2] below 1 K indicates that the pseudogap is strongly suppressed in magnetic field higher than 8 T along the a axis.

In the early stage of the study on CeNiSn,[2] electronic resistivity exponentially increased below 6 K with decreasing temperature. Therefore, CeNiSn was called a ''Kondo semiconductor'' or ''Kondo insulator.'' Recently, Nakamoto and co-workers[6–8] succeeded in drastic amelioration of sample quality of CeNiSn single crystals and showed that the semiconductorlike temperature variation changes to a metallic one with improving the sample quality. Among the typical impurities (Ce_2O_3, $CeNi_2Sn_2$, and $Ce_2Ni_3Sn_2$) in CeNiSn, the amounts of Ce_2O_3 and $CeNi_2Sn_2$ were decreased below the detection limit of electron-probe microanalysis (EPMA) using the Czochralski technique with a hot tungsten crucible baked in a silica tube of the radio-frequency furnace. They found that only the solid-state electrotransport (SSE) treatment can reduce the amount of $Ce_2Ni_3Sn_2$ to less than 0.1%. The SSE treatment for 16 days not only decreases the impurities but also decreases the structural imperfection and strain. In fact, the half width of the rocking curve of neutron-diffraction peaks (200) and (002) were decreased from 3° to 0.4°. Two impurity peaks in specific heat vanished and T-independent value of C/T below 1 K decreased from 57 to 40 mJ/K^2 mol. In the present work, we use the best sample among the single crystals grown with the SSE technique by Nakamoto and co-workers.

The change in the temperature dependence of the resistivity of CeNiSn from the semiconductorlike to the metallic one shows a prominent contrast with the typical Kondo insulators YbB_{12} and $Ce_3Bi_4Pt_3$ for which the increasing ratio of resistivity at low temperatures becomes larger by improving sample quality.[9,10] The semiconductorlike conduction previously observed in CeNiSn is presumably due to carrier localization by impurities and/or imperfection. Ikeda and Miyake[5] showed theoretically that the shape of the gapped DOS around E_F is easily changed by impurity. In fact, the impurities might veil the intrinsic property in early samples. Thus, the sample quality is of essential importance for the study of this material.

Prior to this work, we found clear field dependence of specific heat for high-quality single-crystalline CeNiSn above 2 K in the fields $\mu_0 H$ up to 14 T along the a axis.[11] The field dependence in the temperature range at least above 4 K is well reproduced within the framework of a rigid-band model by assuming the Zeeman splitting of a V-shaped gap with a residual DOS at E_F. At lower temperatures below 3.5 K, however, the calculated value with the rigid DOS model tends to deviate from the experimental data in high field, suggesting that the electronic state around E_F is dynamically changed at lower temperatures by applying magnetic field. The electronic state in a small energy scale should be the intrinsic ground state of CeNiSn. In order to study the detail of the electronic state inside the pseudogap, we have performed specific-heat measurements below 1 K. In this paper, we report the low-temperature specific heat in magnetic field up to 5 T and discuss the ground state in terms of an electronic state formed inside the pseudoenergy gap.

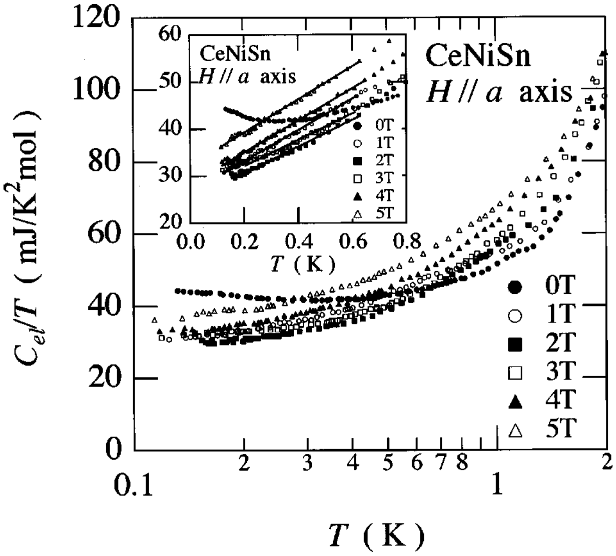

FIG. 1. Electronic specific heat divided by temperature C_{el}/T at selected magnetic fields up to 5 T along the *a* axis. The inset shows temperature dependence of C_{el}/T on a linear scale. The solid lines are guides for the eye.

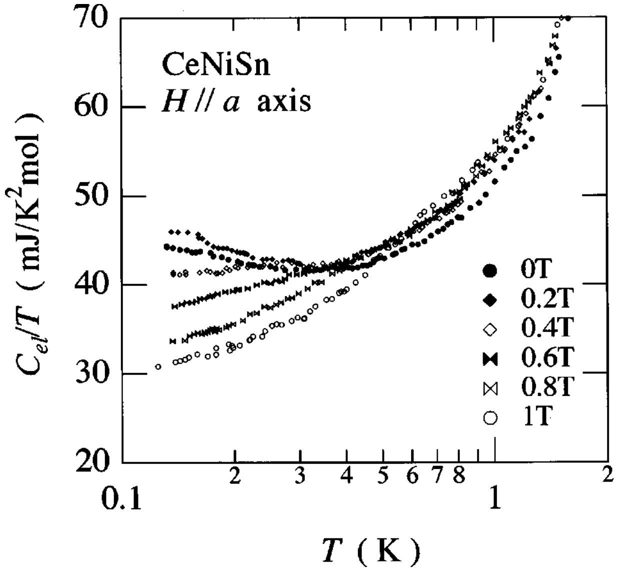

FIG. 2. Low-field part of C_{el}/T plotted as a function of *T*.

II. EXPERIMENT

A single crystal of CeNiSn used in this work was grown by the Czochralski technique using a radio-frequency furnace with a hot tungsten crucible in a purified Ar atmosphere. The sample was purified by a SSE method with current density of 600 $\mathrm{A/cm^2}$ in a vacuum of 1×10^{-9} Torr for 16 days. The surface of the crystal was carefully polished because impurities on the surface results badly. The impurity concentration of Ce_2O_3 and $CeNi_2Sn_2$ in the crystal has been confirmed under the detection limit of the metallographic examination and EPMA and that of $Ce_2Ni_3Sn_2$ has reduced less than 0.1%.[6,8] Details of sample preparation and characterization are described elsewhere.[6] The purified sample shows metallic conduction with the smallest residual resistivity[8] that we have ever obtained, indicating that the sample used in this work is of best quality. Molar specific heat was measured from 0.13 to 2 K in magnetic field up to 5 T using an adiabatic calorimeter suspended from the mixing chamber of a ^{3}He-^{4}He dilution refrigerator via a superconducting heat switch made of Pb.

III. RESULTS AND DISCUSSION

The electronic contribution to specific heat C_{el} was evaluated by subtracting both the nuclear contribution and the phonon contribution from the experimental data. The nuclear contribution C_N is expected from the nuclear spin of ^{61}Ni, ^{115}Sn, ^{117}Sn, and ^{119}Sn. We estimated C_N as specific heat of Schottky-type. The amount of C_N is about 7% of the total specific heat at 0.15 K in the field of 5 T. The phonon contribution C_{ph} was estimated as $C_{ph}=\beta T^3$ by fitting the specific heat of LaNiSn in the absence of field to $C=\gamma T+\beta T^3$ at low temperatures. The values we used are $\gamma=11.4$ mJ/K^2 mol and $\beta=0.49$ mJ/K^4 mol (Ref. 3) and their field dependence was neglected. Figure 1 shows the temperature dependence of C_{el}/T at selected magnetic fields along the *a* axis. With decreasing temperature, C_{el}/T slightly increases below $\sim$ 0.5 K, indicating an enhanced DOS around E_F. With increasing field, C_{el}/T below 0.5 K rapidly decreases and shows a minimum around 2 T. The amount of decrease is more than 30% around 0.15 K at 2 T. After marking the minimum, C_{el}/T increases with the magnetic field. A similar field effect on specific heat has been found in a preliminary work.[12] Such a sensitivity of specific heat to the magnetic field was not observed in low-quality samples[2] in field between 0 and 4 T below 0.8 K. The inset of Fig. 1 shows C_{el}/T below 0.8 K on a linear scale. For $H\geqslant1$ T, C_{el}/T decreases linearly with temperature below 0.6 K. The solid lines in the inset of Fig. 1 are guides for the eye. Except for a very narrow temperature region, we do not see the $\ln T$ dependence of C_{el}/T, which is frequently discussed as a non-Fermi liquid.

Temperature dependence of C_{el}/T between 0 and 1 T are plotted in Fig. 2. The clear field dependence is observed

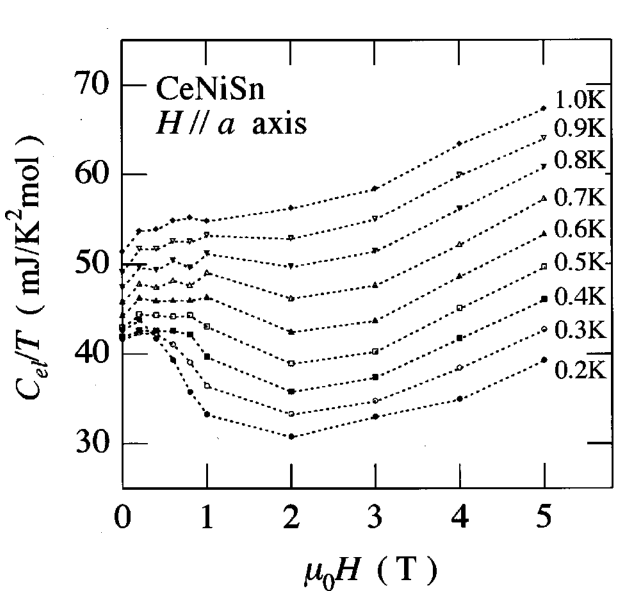

FIG. 3. Magnetic-field dependence of C_{el}/T at various temperatures.

below 0.5 K in contrast with no appreciable field dependence above 0.5 K. As the field increases at a fixed temperature below 0.2 K, C_{el}/T increases and shows a maximum around 0.2 T. With further increasing field, C_{el}/T steeply decreases down to the value at the field of 1 T. The maximum around 0.2 T is possibly due to a fine structure of the DOS.

To show the field dependence more clearly, C_{el}/T is replotted in Fig. 3 as a function of the field at several temperatures. At 0.2 K, C_{el}/T suddenly decreases with increasing field up to 1 T. With further increasing field, the decreasing rate is reduced and C_{el}/T attains a minimum value in a field around 2 T. In higher field, C_{el}/T increases monotonically. As temperature is elevated, the field dependence becomes smooth; especially the low field structure is smeared out around 0.5 K. In the recent work[13] on the longitudinal magnetoresistance along the a axis, a minimum and a peak of Gaussian-type have been found below 0.3 K at 0.2 and 0.77 T, respectively. At the field of 0.2 T where the magnetoresistance shows the minimum, C_{el}/T shows the maximum in its field dependence. Around 0.77 T, the decreasing rate in C_{el}/T becomes a maximum. This close correspondence between magnetoresistance and C_{el}/T in field is attributable to a field-induced change in the DOS.

To explain the unusual enhancement of C_{el}/T below 0.5 K in zero field and substantial decrease in C_{el}/T by applying field, we have tried to fit the data by assuming an additional peak inside a V-shaped pseudogap as illustrated in Fig. 4. The value of $|E_l-E_h|$ is defined to be the width of the residual DOS in this calculation. The field effect is assumed as the Zeeman splitting of the partial DOS, $N^+(E)$ and $N^-(E)$, for the up-spin and down-spin band without a change of the DOS shape. The total DOS, $N(E)$, is calculated as

$$N(E)=N^+(E)+N^-(E), \tag{1}$$

$$N^{\pm}(E)=\frac{A}{\pi}\frac{(D/2)}{(E-E_F\mp E_{\mathrm{Zeeman}})^2+(D/2)^2} \quad \text{for } |E-E_F\mp E_{\mathrm{Zeeman}}|\geqslant\Delta, \tag{2}$$

$$N^{\pm}(E)=\frac{A}{\pi}\left\{\left(N_0-\frac{(D/2)}{\Delta^2+(D/2)^2}\right)\frac{|E-E_F\mp E_{\mathrm{Zeeman}}|-W}{W-\Delta}+N_0\right\} \quad \text{for } W\leqslant|E-E_F\mp E_{\mathrm{Zeeman}}|<\Delta, \tag{3}$$

$$N^{\pm}(E)=-\frac{A}{\pi}\frac{dN}{W}|E-E_F\mp E_{\mathrm{Zeeman}}|+\tilde{N}_0+d\tilde{N} \quad \text{for } |E-E_F\mp E_{\mathrm{Zeeman}}|<W, \tag{4}$$

where D, Δ, and W are the half-widths of the main Lorentzian DOS, the V-shaped pseudogap, and the bottom of the gap, respectively. A normalization factor A is determined so as to satisfy a condition $\int N(E)dE=1$. The parameter $2\tilde{N}_0=2(A/\pi)N_0$ is the residual DOS and $2d\tilde{N}=2(A/\pi)dN$ is the height of the additional peak at the bottom of the pseudogap. The magnitude of the Zeeman splitting is given as $E_{\mathrm{Zeeman}}=\pm g_J|J_z|\mu_B H$ for $N^-(E)$ and $N^+(E)$. Here, g_J, J_z, and

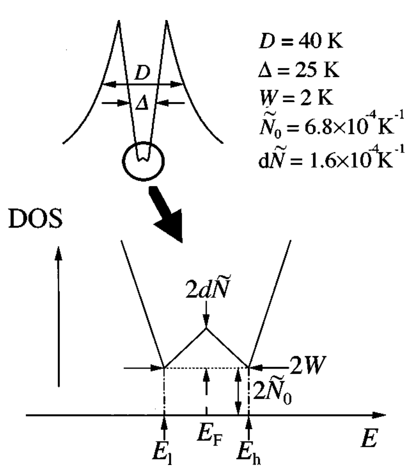

FIG. 4. Schematic DOS with an additional peak structure inside a V-shaped gap. The top figure is the overall DOS. The closeup illustration of the gap bottom is given in the bottom of the figure. The parameters D, Δ, and W are the half-width of the main DOS, the V-shaped gap, and the bottom of the gap, respectively. $2\tilde{N}_0$ and $2d\tilde{N}$ are the magnitude of the residual DOS and the height of the additional peak.

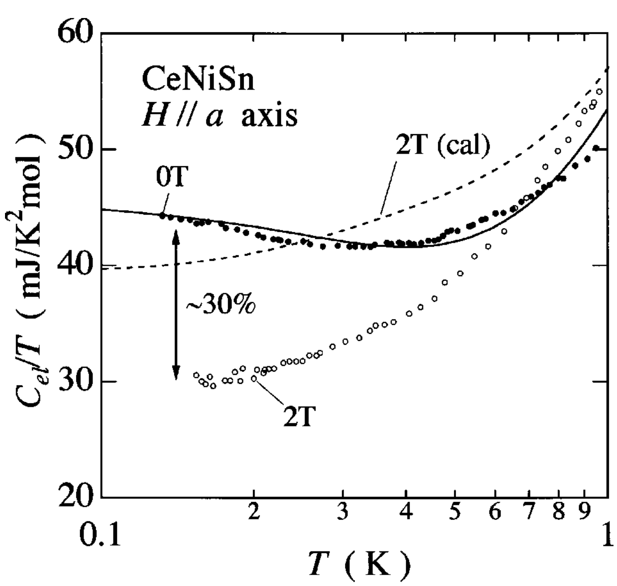

FIG. 5. The fitting by our DOS model. Solid and broken curves represent C_{el}/T calculated for 0 and 2 T, respectively, by using the DOS model shown in Fig. 4.

μ_B are the Landé g factor, the z component of total angular momentum, and the Bohr magneton, respectively. Using the DOS, specific heat is calculated as

$$C_{el}=N_A\int_{-\infty}^{\infty}EN(E)\frac{\partial f(E,T)}{\partial T}dE, \tag{5}$$

where N_A is the Avogadro number and $f(E,T)$ is the Fermi-Dirac distribution function. In this calculation, we have always kept the parameter $g_J|J_z|$ equal to 1.10, which we determined with the specific-heat data above 2 K reported in the previous paper.[11] The fitted results are shown by solid and broken curves in Fig. 5. The zero-field data is well reproduced with the parameters $D=40$ K, $\Delta=25$ K, $W=2.0$ K, $\tilde{N}_0=(A/\pi)N_0=6.8\times10^{-4}$ K^{-1}, and $d\tilde{N}=1.6\times10^{-4}$ K^{-1}, where $N_0=2.5\times10^{-3}$ K^{-1}. Therefore, we have revealed that the DOS of CeNiSn below 0.5 K has the peaked structure inside the pseudogap.

From the Hall-coefficient measurement, a strong decrease of the carrier concentration due to the gap formation has been suggested at low temperatures.[13] The carrier concentration decreases down to 0.0012 /f.u. at 0.5 K if one analyzes the data assuming a one carrier model. Concerning the values of C_{el}/T and the carrier concentration, we can roughly estimate the Sommerfeld coefficient per one carrier of $\sim10^4$ mJ/K^2 mol. This argument strongly suggests that the electronic state in the bottom of the pseudogap consists of a renormalized quasiparticle with enhanced effective mass due to a many-body effect.

In contrast with the successful fitting for zero field, the broken curve calculated for 2 T deviates remarkably from the experimental data with 30% reduction in C_{el}/T at 0.2 K, so long as the same parameter of $g_J|J_z|=1.10$ is used and the Zeeman splitting of the rigid partial bands is assumed. The theory by Ikeda and Miyake,[5] which well reproduces previous experimental results,[3,8,14,6] predicted that neither the DOS around E_F is enhanced at low temperatures nor the DOS is drastically suppressed by the field. Hence, the electronic property of CeNiSn is likely governed by a many-body effect, which first forms a Kondo resonance peak, then a pseudogap at E_F, and finally a new quasiparticle state with small characteristic energy at the bottom of the gap as temperature is lowered. The peak formed in DOS below 0.5 K, if it is intrinsic, is possibly an indication for a new-type metallic ground state in CeNiSn.

Considering the energy scale of the new ground state, the electronic state should have a characteristic temperature $T^*\leqslant1$ K since C_{el}/T increases below 0.5 K at zero field. The characteristic temperature $T^*\sim1$ K corresponds to the Zeeman energy $E_{\mathrm{Zeeman}}/k_B=g_J|J_z|\mu_B H/k_B$ for 1 T. It is quite reasonable that the new electronic state around E_F is dynamically destroyed by the magnetic field of ~1 T. Thus, the initial decrease in C_{el}/T can be interpreted as the suppression of the new electronic state by field. The increase in C_{el}/T above 2 T is reasonably explained by the overlap of the regions above E_h and below E_l in our DOS model (Fig. 4) due to the Zeeman splitting. The initial decrease in C_{el}/T has not been found above 1 K probably because the additional peak structure in the DOS vanishes above 0.5 K. The T-linear dependence of C_{el}/T above 1 T suggests that the DOS is proportional to $|E_F-E|$ above 1 T.

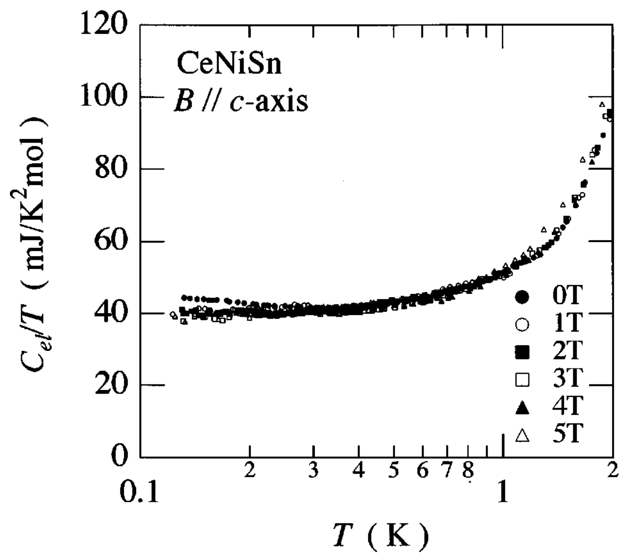

FIG. 6. Temperature dependence of C_{el}/T for $H\|c$, which shows weak-field dependence.

In the above discussion, the new peak in the DOS was assumed as a new intrinsic state of CeNiSn. We must examine possibilities that the peak arises from any extrinsic origin. One of the most likely cases is that an impurity band is responsible for the T and H dependence of C_{el}/T. However, the upturn of C_{el}/T below 0.5 K at zero field becomes clearer with purifying the crystal, suggesting that the low-temperature enhancement in specific heat is unlikely to result from impurities. The remarkable field effect was observed below 4 T for the high-quality crystal in this work. No field dependence was observed in specific heat for low-quality samples.[2] The impurities might blur the quasiparticle band so as to veil the field dependence of specific heat. We also measured the specific heat for $H\|c$. The results for several fields are plotted in Fig. 6. In contrast with the case for $H\|a$, no significant reduction in C_{el}/T was observed from 0.13 to 2 K even at 5 T. This strongly anisotropic field dependence agrees well with the behavior above 2 K in which the significant field effect is found only for $H\|a$ not for $H\|b$ or $H\|c$. If the low-temperature upturn in C_{el}/T arises from impurities, isotropic field dependence is expected because the randomness introduced by the impurities make the Fermi surface more isotropic. Thus, it is difficult to explain the strongly anisotropic field dependence of C_{el}/T by impurities. We believe that our findings are an intrinsic property of CeNiSn.

IV. CONCLUSION

We have observed for high-quality single-crystalline CeNiSn the unusual upturn of C_{el}/T below 0.5 K as well as the strong suppression of low-temperature specific heat in field below 1 T applied along the *a* axis. The *T* and *H* dependence suggests a growth of a new electronic state due to a many-body effect inside the pseudogap at low temperatures. From this fact, we propose that CeNiSn is a different type of strongly correlated metal although this compound has been classified as a Kondo insulator so far.

ACKNOWLEDGMENTS

We thank Professor K. Miyake for valuable discussions and Y. Matsumoto for his technical support. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

[1] I. Higashi, K. Kobayashi, T. Takabatake, and M. Kawaya, J. Alloys Compd. **193**, 300 (1993).

[2] T. Takabatake, M. Nagasawa, H. Fujii, G. Kido, M. Nohara, S. Nishigori, T. Suzuki, T. Fujita, R. Helfrish, U. Ahlheim, K. Fraas, C. Geibel, and F. Steglich, Phys. Rev. B **45**, 5740 (1992).

[3] S. Nishigori, H. Goshima, T. Suzuki, T. Fujita, G. Nakamoto, H. Tanaka, T. Takabatake, and H. Fujii, J. Phys. Soc. Jpn. **65**, 2614 (1996).

[4] M. Kyogaku, Y. Kitaoka, H. Nakamura, K. Asayama, T. Takabatake, F. Teshima, and H. Fujii, J. Phys. Soc. Jpn. **59**, 1728 (1990).

[5] H. Ikeda and K. Miyake, J. Phys. Soc. Jpn. **65**, 1769 (1996).

[6] G. Nakamoto, T. Takabatake, H. Fujii, A. Minami, K. Maezawa, I. Oguro, and A. A. Menovsky, J. Phys. Soc. Jpn. **64**, 4834 (1995).

[7] G. Nakamoto, T. Takabatake, Y. Bando, H. Fujii, K. Izawa, T. Suzuki, T. Fujita, A. Minami, I. Oguro, L. T. Tai, and A. A. Menovsky, Physica B **206-207**, 840 (1995).

[8] T. Takabatake, G. Nakamoto, T. Yoshino, H. Fujii, K. Izawa, S. Nishigori, H. Goshima, T. Suzuki, T. Fujita, K. Maezawa, T. Hiraoka, Y. Okayama, I. Oguro, A. A. Menovsky, K. Neumaier, A. Brückl, and K. Andres, Physica B **223-224**, 413 (1996).

[9] F. Iga, N. Shimizu, and T. Takabatake, J. Magn. Magn. Mater. **177-181**, 337 (1998).

[10] J. C. Cooley, M. C. Aronson, and P. C. Canfield, Phys. Rev. B **55**, 7533 (1997).

[11] K. Izawa, T. Suzuki, M. Kitamura, T. Fujita, T. Takabatake, G. Nakamoto, H. Fujii, and K. Maezawa, J. Phys. Soc. Jpn. **65**, 3119 (1996).

[12] K. Andres and T Takabatake (private communication).

[13] T. Takabatake, F. Iga, T. Yoshino, Y. Echizen, K. Kobayashi, M. Higa, K. Katoh, N. Shimizu, Y. Bando, G. Nakamoto, H. Fujii, K. Izawa, T. Suzuki, T. Fujita, M. Sera, M. Hiroi, K. Maezawa, S. Mock, H. v. Löneysen, A. Bückl, K. Neumaier, and K. Andres, J. Magn. Magn. Mater. **177-181**, 277 (1998).

[14] K. Nakamura, Y. Kitaoka, K. Asayama, T. Takabatake, G. Nakamoto, H. Tanaka, and H. Fujii, Physica B **206-207**, 829 (1995).