Magnetic and transport properties of the mixed-valent compound $YbRh_2Ga$

G. F. Chen,* I. Sakamoto, and S. Ohara
Department of Electrical & Computer Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

T. Takami, H. Ikuta, and U. Mizutani
Department of Applied Physics, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
(Received 23 June 2003; published 27 February 2004)

We report the measurements of specific heat, electrical resistivity, magnetic susceptibility, Hall coefficient and thermoelectric power on a ternary compound of $YbRh_2Ga$, which crystallizes in the triple-hexagonal Na_3As-type structure with the space group $P6_3$ cm. $YbRh_2Ga$ remains in a paramagnetic state down to 1.2 K. The magnetic susceptibility exhibits a broad maximum around 90 K for $H\|c$ or 170 K for $H\perp c$, respectively. Such maximum is a characteristic of the Ce- and Yb-based mixed-valent compounds. The temperature dependence of electrical resistivity shows an *S*-type behavior. The electronic specific heat coefficient is 36.6 $mJ/molK^2$, which is nine times larger than that of YRh_2Ga (3.9 $mJ/molK^2$) with no $4f$ electron. The thermoelectric power ($\Delta T\|c$) shows a broad minimum at about 120 K with a relatively large negative value, ~ -36 $\mu V/K$, which is typical for Yb-based spin-fluctuation systems. The Hall coefficient ($J\|c, H\perp c$) exhibits a maximum around 60 K; at higher temperatures it varies with temperature in a manner suggestive of skew scattering. All of the measurement results indicate that $YbRh_2Ga$ is a typical mixed-valent system. The anisotropy observed in $YbRh_2Ga$ indicates anisotropic hybridization between localized $4f$-electron and conduction elections.

DOI: 10.1103/PhysRevB.69.054435 PACS number(s): 75.30.Mb, 71.27.+a, 75.20.Hr

I. INTRODUCTION

It is well known that some Ce-, Sm-, Eu-, and Yb-based intermetallic compounds exhibit mixed-valent or valence-fluctuating behaviors.[1,2] The unconventional behaviors are reflected in unit-cell volume, static dc susceptibility, electrical resistivity, etc., and are thought to result from the proximity between the energy level of the $4f$ electrons to the Fermi level and the resulting hybridization between these electrons. Recently, the new ternary compound of $YbIr_2Ga$ with a quasi-two-dimensional (2D) structure was characterized to be in a mixed-valent state.[3] The electronic specific heat is as large 21.7 $mJ/molK^2$ and the magnetic susceptibility shows a broad maximum near 180 K ($H\|c$) or 250 K ($H\perp c$), respectively. However, the electrical resistivity was found to be featureless. In order to further understand the formation of the mixed-valent behavior with nonmagnetic ground state in this quasi-2D system, we try to grow the single crystal of $YbRh_2Ga$ and measure the physical properties. Here we report our preliminary results of magnetic susceptibility, specific heat, electrical resistivity, Hall coefficient and thermoelectric power in $YbRh_2Ga$. We found that $YbRh_2Ga$ shows a pronounced mixed-valent or valence-fluctuating behavior. It is rather uncommon to find mixed-valent behavior in noncubic systems.

II. EXPERIMENT

The single crystals of $YbRh_2Ga$ were grown from a Ga-flux.[3] The obtained crystals were characterized by a powder x-ray diffraction method using Cu–K_α radiation at room temperature. The dc electrical resistivity and Hall coefficient measurements were performed by standard four- and five-probe methods, respectively, between 1.5 K and room temperature. The specific heat was measured by the relaxation method in zero field and in 8 T in the temperature range from 1.2 to 40 K. The magnetic susceptibility measurements were carried out in a magnetic field of 0.5 T between 1.8 and 390 K using the quantum design (SQUID) magnetometer. The thermoelectric power was measured between 2 K and room temperature using a four-wire dynamic method. All measurements were performed on the well-polished samples.

III. RESULTS AND DISCUSSION

The power x-ray diffraction pattern of $YbRh_2Ga$ single crystals shows that the sample crystallizes in the triple-hexagonal Na_3As-type structure with the space group $P6_3$ cm.[3,4] No traces of secondary phases were observed. The crystal structure can be described as a layered quasi-2D structure,[3] in which Yb–Ga layers are separated by Rh layers stacked along the c axis. This structure indicates that $YbRh_2Ga$ should have a large anisotropy in physical properties. The lattice parameters for $YbRh_2Ga$ are $a=7.483\pm0.002$ Å and $c=9.461\pm0.003$ Å, obtained by a least-squares fit to the experimental data. Figure 1 shows a plot of the unit-cell volume vs rare-earth elements (Gd–Lu).[5] A volume anomaly appears for $YbRh_2Ga$, which suggests the divalent or intermediate state of the Yb ions.

Figure 2 shows the temperature dependence of magnetic susceptibility with magnetic field H (=0.5 T) applied parallel or perpendicular to c axis in the temperature range 1.8–390 K. The susceptibility $\chi_\|$ ($H\|c$) is much larger than $\chi_\perp$ ($H\perp c$) in all of the measured temperature range. This strong anisotropy is thought to be due to anisotropic c-f mixing interaction[6] along the a and c axis of the hexagonal

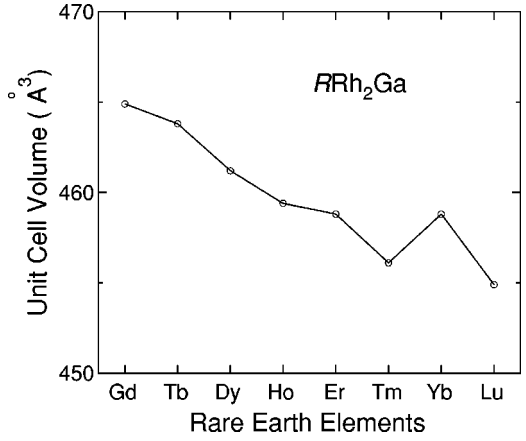

FIG. 1. Unit-cell volume vs rare-earth element in $R\mathrm{Rh}_2\mathrm{Ga}$ compounds.

Na_3As-type structure. The distinctive feature of $\chi(T)$ curves is a broad maximum at $T_{\max,\chi}\approx 90$ K for $H\|c$ and $T_{\max,\chi}\approx 170$ K for $H\perp c$, respectively. The high temperature scales, $T_{\max,\chi}\sim 100$ K, are typical of mixed-valent compounds with Kondo temperature T_K greater than 500 K.[1,2] No impurity trail was observed in the susceptibility of $YbRh_2Ga$ at the lowest temperatures, indicating the high quality of our sample. Above 250 K, $\chi_{\|}(T)$ follows Curie–Weiss law, $\chi(T)=N\mu_{\mathrm{eff}}^2/3\kappa_{\mathrm{B}}(T-\Theta)$, and gives effective moment $\mu_{\mathrm{eff}}=3.43\ \mu_{\mathrm{B}}$ and Weiss temperature $\Theta=-40$ K. The value of effective moment is reduced from 4.54 μ_{B} expected for free Yb^{3+} ions, which indicates an intermediate valence state of the Yb ions in $YbRh_2Ga$. But $\chi_{\perp}(T)$ does not exhibit Curie–Weiss behavior up to 390 K. According to the Bethe-ansatz solution of Coqblin–Schrieffer model for Kondo-impurity system,[7] the characteristic spin-fluctuation temperature T_0 could be estimated from

$$T_0=\nu(\nu^2-1)(g\mu_{\mathrm{B}})^2/24k_{\mathrm{B}}\chi(0), \tag{1}$$

where ν is the magnetic degeneracy, g is the Landé g factor, μ_{B} is the Bohr magneton, and k_{B} is Boltzmann's constant.

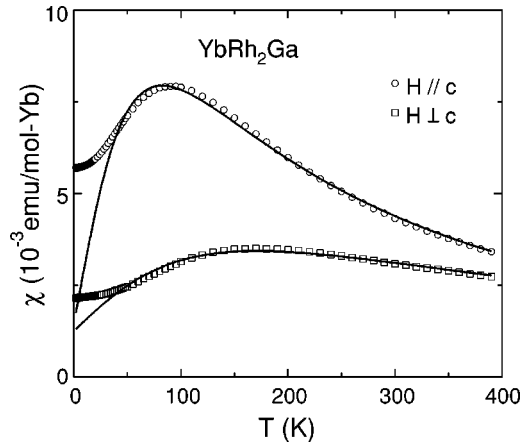

FIG. 2. Temperature dependence of magnetic susceptibility for $YbRh_2Ga$ with magnetic field ($H=0.5$ T) applied parallel or perpendicular to c axis. The solid lines are the fits of χ to the ICF model with the parameters given in the text.

$\chi(0)$ is estimated to be 5.68×10^{-3} emu/mol for $H\|c$ or 2.14×10^{-3} emu/mol for $H\perp c$, respectively. Taking $\nu=8$ and $g=8/7$, we get the characteristic temperature $T_0=577$ K for $H\|c$ or 1532 K for $H\perp c$, respectively, which is comparable to the value $T_0=824$ K obtained by using the equation $C/T(T\rightarrow0)=\gamma=(\nu-1)\pi\kappa_{\mathrm{B}}/6T_0$, and $\gamma=36.6$ mJ/molK^2 given in later. Rajan[7] had given the temperature dependence of magnetic susceptibility in terms of the Bethe-ansatz solution of the Coqblin–Schrieffer model. We have tried to fit experimental data using the obtained parameters. However, in this case, the theoretical curves of $\chi(T)$ do not reproduce the experimental results well (not shown here). The disagreement may be attributed to the valency of Yb ions in $YbRh_2Ga$, which deviates strongly from +3; this point can be understood from the relatively small effective moment value. Bickers *et al.*[8] have calculated the temperature dependence of magnetic susceptibility with the $4f$ occupation number $n_f<1$ for $\nu=6$ and found that $\chi(T)$ deviates strongly from the case $n_f=1$.

An alternative approach describing the features of intermediate valence systems is the interconfiguration fluctuation (ICF) model.[9] In the ICF model, the interaction of the conduction electrons with the $4f$ shell induces that the rare earth ion fluctuates between two configurations: ground state and excited state. The magnetic susceptibility of Yb ions in the ICF model can be written as

$$\chi=N(4.54\mu_{\mathrm{B}})^2\upsilon(T)/3\kappa_{\mathrm{B}}(T+T_{sf})+\chi_0 \tag{2}$$

and

$$\upsilon(T)=8/\{8+\exp[-E_{\mathrm{ex}}/\kappa_{\mathrm{B}}(T+T_{sf})]\}, \tag{3}$$

where E_{ex} is the energy difference between the $4f^{14}$ and $4f^{13}$ states, and T_{sf} is spin-fluctuation temperature, χ_0 is the temperature independent susceptibility. The fits of the measured data to Eqs. (2) and (3) are in reasonable agreement in the high temperature region and give $-E_{\mathrm{ex}}/k_{\mathrm{B}}=294$ K, $T_{sf}=62$ K and $\chi_0=-9.3\times10^{-4}$ emu/mol for $H\|c$, or $-E_{\mathrm{ex}}/k_{\mathrm{B}}=684$ K, $T_{sf}=164$ K, and $\chi_0=-4.8\times10^{-4}$ emu/mol for $H\perp c$, respectively. The large negative E_{ex} values indicate that the magnetic $4f^{13}$ state is situated well above the nonmagnetic $4f^{14}$ ground state. The values of E_{ex} and T_{sf} are comparable to those of well-known Yb-based compounds like $YbAl_3$.[9] The valence of Yb ion estimated from Eq. (3) is 2.78 for $H\|c$ or 2.65 for $H\perp c$ at room temperature.

The temperature dependence of electrical resistivity measured with the current J parallel or perpendicular to c axis is shown in Fig. 3. The electrical resistivity increases monotonically with temperatures up to room temperature. A broad shoulder was observed at $\sim$150 K for both directions. This temperature dependence resembles that of typical Yb-based mixed-valent compounds such as $YbAl_3$, which possesses a characteristic temperature $T_K\sim670$ K.[1,10] This relatively large T_K value is expected to overcome the crystal-electric-field (CEF) splitting. In $YbRh_2Ga$, $\rho_{\|}$ ($J\|c$) is much larger than $\rho_{\perp}$ ($J\perp c$) over all the temperatures, suggesting the high anisotropy. This anisotropy in ρ could be also considered to result from the anisotropic hybridization between localized

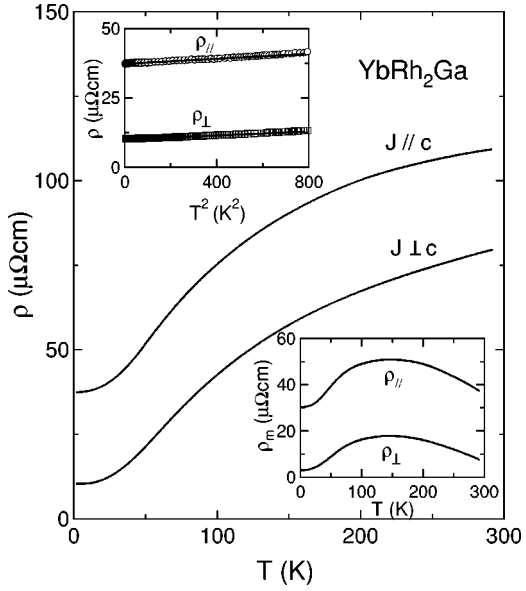

FIG. 3. Temperature dependence of electrical resistivity of $YbRh_2Ga$ with the current parallel or perpendicular to c axis between 1.6 K and room temperature. Upper inset: The electrical resistivity vs quadratic temperature in low temperature region. The solid line shows the T^2 dependence. Lower inset: Magnetic contribution to the resistivity of $YbRh_2Ga$ as a function of temperature obtained by subtracting the resistivity of YRh_2Ga.

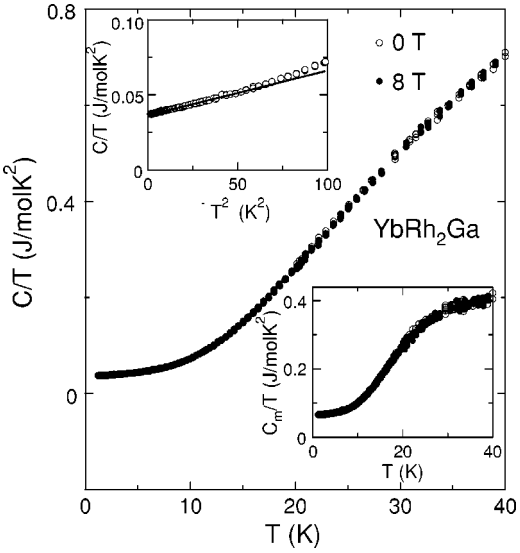

FIG. 4. Specific heat divided by temperature C/T vs temperature T for $YbRh_2Ga$ between 1.2 and 40 K in applied magnetic fields H of 0 and 8 T ($H \| c$). Upper inset: Specific heat divided by temperature C/T vs T^2 at $H=0$. The solid line is a fit of $C/T=\gamma+\beta T^2$ with the parameters given in the text. Lower inset: Magnetic contribution to the specific heat in $YbRh_2Ga$.

$4f$-electron and conduction elections.[6] At room temperature, $\rho_\parallel$ is 110 $\mu\Omega$cm and $\rho_\perp$ is 80 $\mu\Omega$cm, respectively, which is the same order of magnitude as other known mixed-valent compounds.[1,2] As shown in the upper inset of Fig. 3, ρ shows a T^2-dependence up to 25 K, indicative of Fermi-liquid behavior or spin fluctuations. The fit of equation $\rho=\rho_0+AT^2$ to the data yields the residual resistivity $\rho_0=37.42$ $\mu\Omega$cm (10.21 $\mu\Omega$cm) and $A=0.0047$ $\mu\Omega$cm/K^2 (0.0033 $\mu\Omega$cm/K^2) for $J \| c$ ($J \perp c$), respectively. The A value along c axis is larger than that perpendicular to c axis. To estimate the magnetic contribution ρ_m to the electrical resistivity, we use the data of YRh_2Ga as a reference material (not shown here). We assumed that the temperature dependence of resistivity of YRh_2Ga represents the phonon contribution to the resistivity of $YbRh_2Ga$ and the residual resistivity is approximately the same in both compounds, and then we get $\rho_m=\rho_{\mathrm{Yb}}-\rho_{\mathrm{Y}}$. The obtained ρ_m vs T was plotted in the lower inset of Fig. 3. The prominent feature of the magnetic resistivity is the presence of a broad maximum at $T_{\max,\rho m}\approx 150$ K. Similar behaviors have been observed in many valence-fluctuating systems.[1,11,12] In most of the cases, the temperature scale of this transport anomaly is comparable to $T_{\max,\chi}$ deduced from the magnetic susceptibility. Since $T_{\max,\chi}$ can be chosen as an order of magnitude estimate of the Ce (Yb) spin fluctuation temperature, it is natural to attribute the anomaly of resistivity to a strong Ce (Yb) spin-scattering for those compounds where $T_{\max,\rho m}\approx T_{\max,\chi}$.[1] In $YbRh_2Ga$, $T_{\max,\chi}$ values are also comparable to $T_{\max,\rho m}$, and so we suggest that the transport anomaly should be accounted for by the spin-scattering mechanism, rather than the CEF splitting or Kondo scattering mechanism.

Figure 4 plots the specific heat divided by temperature C/T vs T between 1.2 and 40 K measured in zero field and in 8 T. The absence of an anomaly in $C(T)$ for $YbRh_2Ga$ confirms that this compound does not exhibit any magnetic order, at least down to 1.2 K. The upper inset shows the plots of C/T vs T^2 in zero field. A linear dependence of C/T on T^2 was observed up to 8 K. Fitting the data to the expression $C/T=\gamma+\beta T^2$ gives $\gamma=36.6$ mJ/molK^2, $\beta=0.306$ mJ/molK^4, and Debye temperature $\theta_{\mathrm{D}}=294$ K. The γ value is nine times larger than that of YRh_2Ga (3.9 mJ/molK^2, not shown here) with no $4f$ electron and small larger than that of isostructural compound $YbIr_2Ga$.[3] The enhanced value for $YbRh_2Ga$ is comparable to those of known intermediate compounds: $\gamma=45$ mJ/molK^2 for $YbAl_3$,[13] $\gamma=135$ mJ/molK^2 for $YbCu_2Si_2$,[14] and $\gamma=260$ mJ/molK^2 for YbCuAl.[15] The enhancement of the electronic specific heat in $YbRh_2Ga$ indicates that the electronic state of the Yb ions is likely in valence fluctuating state rather than in a tri-valent state. In heavy-fermion systems, magnetic fields are expected to cause important changes, especially for the low-temperature specific heat. For example, in $YbAgCu_4$,[16] γ increases strongly with field (by 10% at 10 T) and shows a quadratic field dependence up to 10 T. However, in our case, no distinct difference was observed between the specific heat measured in zero field and in 8 T as shown in the Fig. 4. A very small enhancement (0.1 mJ/molK^2) is consistent with the not enough large value of γ. The magnetic contribution $C_m(T)$ to specific heat for $YbRh_2Ga$ was deduced by subtracting $C(T)$ of YRh_2Ga, as plotted in the lower inset of Fig. 4. No anomaly was observed at low temperatures. Note that a maximum or increase of C_m/T at the lowest temperatures was frequently observed in some mixed-valent compounds where a second energy

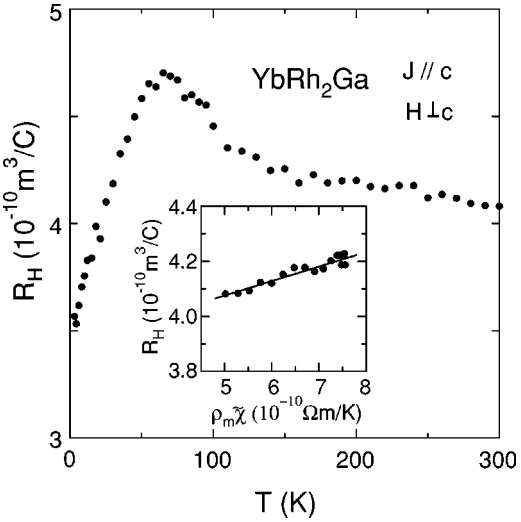

FIG. 5. Temperature dependence of Hall coefficient R_H for $YbRh_2Ga$ with current along c axis and magnetic field applied perpendicular to c axis. Inset: Hall coefficient R_H plotted as $\rho_m\tilde{\chi}$. The solid line shows the linear dependence.

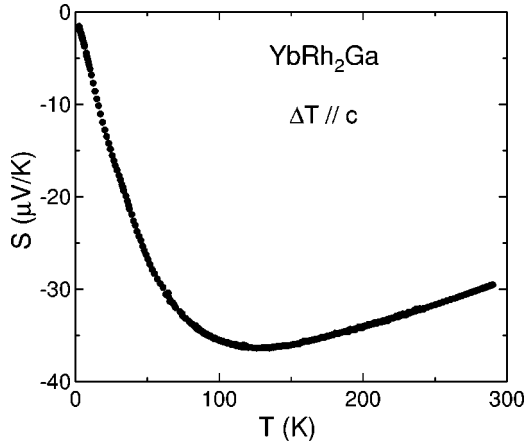

FIG. 6. Plots of thermoelectric power S vs temperature T for $YbRh_2Ga$ with thermal gradient parallel to c axis.

scale was developed, like $YbAl_3$[10] and $CeNiSi_2$.[17] The estimated magnetic entropy S_m is close to $R\ln 2$ per Yb ion at 40 K.

For comparison with other heavy-fermion and mixed-valent compounds, we estimated the Kadowaki–Woods ration[18] A/γ^2 for $YbRh_2Ga$, where A is the coefficient of the T^2-term of the electrical resistivity and γ is the electronic contribution to the specific heat. The values of A/γ^2 are 0.3×10^{-5} $\mu\Omega$cm/(molK/mJ)^2 for $J\|c$ or 0.24×10^{-5} $\mu\Omega$cm/(molK/mJ)^2 for $J\perp c$, respectively. These values are the same order as the common value of 1×10^{-5} $\mu\Omega$cm/(molK/mJ)^2 for other mixed-valent compounds, like $YbAl_3$,[19] which is estimated to be 0.4×10^{-5} $\mu\Omega$cm/(molK/mJ)^2. This result confirmed that $YbRh_2Ga$ is a typical mixed-valent compound.

Figure 5 shows the Hall coefficient R_H vs temperature T for $YbRh_2Ga$ between 2 and 300 K measured with $J\|c$ and $H\perp c$ ($H=1.3$ T). R_H is positive over the measured temperature range. With decreasing temperature, R_H increases and exhibits a maximum around 65 K and followed by steep decrease toward lower temperatures. In the impurity Kondo system, the Hall coefficient can be described by the expression[20–22]

$$R_H = R_0 + \gamma^* \rho_m \tilde{\chi}, \tag{4}$$

where R_0 is the ordinary Hall constant, $\tilde{\chi}$ is the reduced susceptibility, $\tilde{\chi}=\chi/C$ (where C is the Curie constant), γ^* is a constant and ρ_m is magnetic resistivity. The second term, the anomalous Hall coefficient, arises from skew scattering of conduction electrons by Yb ions. We have tried to fit the data by using the Eq. (4). We plotted the R_H vs $\rho_m\tilde{\chi}$ in the inset of Fig. 5 in the temperature range 140–300 K. The linear dependence, shown by the solid line, gives $R_0=3.86$ 10^{-10} m^3/C and $\gamma^*=0.046$ K/T. The γ^* value is comparable to those of heavy-fermion or mixed-valent compounds.[20]

The temperature dependence of thermoelectric power S for $YbRh_2Ga$ with thermal gradient parallel to c axis is shown in Fig. 6. In contrast to R_H, S is negative at all temperatures. The prominent feature in the thermoelectric power is the large absolute value (~ -29 μV/K at room temperature) which exceeds those of simple metals by one or two orders magnitude, and exhibits a broad minimum at $T_{\min,S}\approx 120$ K, where $S\approx -36$ μV/K. We found that $T_{\min,S}$ is close to $T_{\max,\chi}$ where the magnetic susceptibility shows a broad maximum. Note that the broad negative anomaly agrees with those observed in most of Yb-based mixed-valent compounds.[23] It is opposite in sign to the Ce compounds due to the electron-hole symmetry of Ce^{3+} $4f^1$ compared with Yb^{3+} $4f^{13}$.

In summary, our results indicate that $YbRh_2Ga$ is a typical mixed-valent system with a magnetically nonordered ground state. This compound offers an interesting example of mixed valence in noncubic systems. The anisotropy observed in $YbRh_2Ga$ could be attributed to the anisotropic c-f mixing along a and c axis of the hexagonal Na_3As-type structure. To understand better the anisotropic anomaly in $YbRh_2Ga$, it is necessary to obtain detailed information[6] on the electronic structure near the Fermi surface.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Biwa and Mr. Kamatani for their assistance in the specific heat measurements.

*Author to whom correspondence should be addressed. Department of Electrical & Computer Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan. Email address: r04elc07@edsys.center.nitech.ac.jp

[1] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[2] P. Wachter, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (Elsevier, Amsterdam, 1994), Vol. 19, Lanthanides/Actinides: Physics—II, p. 177.

[3] C. Petrovic, M. F. Hundley, R. Movshovich, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, Z. Fisk, A. Garcia, E. Granado, I. Torriani, and C. Rettori, J. Magn. Magn. Mater. **225**, 317 (2001); C. Petrovic, M. F. Hundley, R. Movshovich, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, and Z. Fisk, J. Alloys Compd. **325**, 1 (2001).

[4] P. Hafner and K. J. Range, J. Alloys Compd. **216**, 7 (1994); K. J. Range, R. Ehrl, and P. Hafner, *ibid.* **240**, 19 (1996).

[5] G. F. Chen, S. Ohara, and I. Sakamoto (unpublished).

[6] See, for example, B. R. Cooper, R. Siemann, D. Yang, P. Thayamballi, and A. Banerjea, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (Elsevier, New York, 1985), Vol. 2, p. 415; B. R. Cooper, J. M. Wills, N. Kioussis, and Q. G. Sheng, J. Appl. Phys. **64**, 5587 (1988); S. Zhang and P. M. Levy, Phys. Rev. B **40**, 7179 (1989); P. M. Levy and S. Zhang, Phys. Rev. Lett. **62**, 78 (1983).

[7] V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[8] N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B **36**, 2036 (1987).

[9] B. C. Sales and D. K. Wohlleben, Phys. Rev. Lett. **35**, 1240 (1975).

[10] A. L. Comelius, J. M. Lawrence, T. Ebihara, P. S. Riseborough, C. H. Booth, M. F. Hundley, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, M. H. Jung, A. H. Lacerda, and G. H. Kwei, Phys. Rev. Lett. **88**, 117201 (2002).

[11] W. H. Lee, H. C. Ku, and R. N. Shelton, Phys. Rev. B **36**, 5739 (1987).

[12] D. T. Adroja, S. K. Malik, B. D. Padalia, and R. Vijayaraghavan, Phys. Rev. B **39**, 4831 (1989).

[13] E. E. Havinga, K. H. Buschow, and H. J. van Daal, Solid State Commun. **13**, 621 (1973).

[14] B. C. Sales and R. Viswanathan, J. Low Temp. Phys. **23**, 449 (1976).

[15] R. Pott, R. Schefzyk, D. Wohlleben, and A. Junod, Z. Phys. B: Condens. Matter **44**, 17 (1984).

[16] T. Graf, J. M. Lawrence, M. F. Hundley, J. D. Thompson, A. Lacerda, E. Haanappel, M. S. Torikachvili, Z. Fisk, and P. C. Canfield, Phys. Rev. B **51**, 15053 (1995).

[17] E. D. Mun, Y. S. Kwon, and M. H. Jung, Phys. Rev. B **67**, 033103 (2003).

[18] K. Kadowaki and S. B. Woods, Solid State Commun. **58**, 507 (1986).

[19] S. Ohara, G. F. Chen, and I. Sakamoto, J. Alloys Compd. **323–324**, 632 (2001).

[20] A. Fert and P. M. Levy, Phys. Rev. B **36**, 1907 (1987).

[21] P. Coleman, P. W. Anderson, and T. V. Ramakrishnan, Phys. Rev. Lett. **55**, 414 (1985).

[22] E. Cattaneo, Z. Phys. B: Condens. Matter **64**, 317 (1986).

[23] See, for example, E. Bauer, Adv. Phys. **40**, 417 (1991).