Thermal Expansion and Magnetostriction of YbAuCu$_4$

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Abstract
Precise thermal expansion and magnetostriction measurements were performed on the heavy-fermion compound YbAuCu$_4$ in order to examine the crossover valence transition at $T_v$ which was proposed by the nuclear magnetic resonance measurements. The temperature dependence of the thermal expansion coefficient $\alpha$ under magnetic fields shows a broad peak, which shifts to higher temperatures with increasing magnetic fields. The corresponding linear thermal expansion $\Delta \ell / \ell$ parallel to the magnetic field of 7.0 T shows a marked decrease below about 10 K, indicating a contraction of sample length at low temperatures. These results are discussed in relation to the observed temperature dependence of the nuclear quadrupole frequency $\nu_Q$ under magnetic fields.

Keywords: Thermal expansion, Magnetostriction, YbAuCu$_4$

1 Introduction

The $f$ electrons of rare earth and actinide compounds are typical in exhibiting a variety of characteristic properties such as heavy fermions, metamagnetic transitions, non-Fermi liquid behavior, and anisotropic superconductivity in the vicinity of a quantum critical point [1, 2]. These phenomena have been discussed on the basis of the Doniach phase diagram [3], and can be understood as competitive phenomena between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect. Here, spin fluctuations at the magnetic quantum critical point play important roles. Recently, new trends of quantum critical phenomena have been observed in some Yb-based heavy-fermion compounds, such as YbRh$_2$Si$_2$ [4] and YbAlB$_4$ [5], which do not follow the conventional spin fluctuation theory [6, 7, 8]. Watanabe et al. recently suggested that critical valence fluctuations of Yb ions are the key origin of emergence of these new type...
Figure 1: (a) Temperature dependences of the specific heat of YbAuCu$_4$ under several magnetic fields and (b) the electrical resistivity in the logarithmic temperature scale.

of quantum criticality [9]. The ternary intermetallic compound YbInCu$_4$ is known as a typical Yb-based compound that exhibits the first-order valence transition at $T = 42$ K [11]. Theory suggests that valence fluctuations diverge at the critical end point of the first-order valence transition, and when the critical end point is suppressed by tuning material parameters, new quantum critical phenomena emerge around the quantum critical end point [10].

YbAuCu$_4$ is one of the sister compounds of YbInCu$_4$. It crystallizes in the AuBe$_5$-type (space group $F\overline{4}3m$) cubic structure and shows a large electronic specific heat coefficient larger than 2 J/(K$^2$·mol) at low temperatures [12, 13, 14]. Antiferromagnetic order appears below $T_N \simeq 0.6$ K with the ordered magnetic moment of 0.85 $\mu_B$/Yb, which is substantially reduced with respect to that expected for the $\Gamma_7$ ground state doublet, 1.71 $\mu_B$/Yb [15]. The specific heat measurements revealed that the entropy release at $T_N$ is only 30-40% of $R \ln 2$ [12]. Crystalline electric field (CEF) excitations were observed by neutron scattering experiments, and the excitation energies were determined as $\Gamma_7$(0 K)-$\Gamma_8$(45 K)-$\Gamma_6$(80 K) [16].

Very recently, quantum criticality of YbAuCu$_4$ was studied by the electrical resistivity, nuclear quadrupolar resonance (NQR) and nuclear magnetic resonance (NMR) measurements [17, 18]. Magnetic fields can drive the antiferromagnetically ordered state to a non-magnetic Fermi liquid state through a field-tuned quantum critical point at $\mu_0 H_c \simeq 1.3$ T. The obtained magnetic field versus temperature ($H-T$) phase diagram of YbAuCu$_4$ is very similar to that of YbRh$_2$Si$_2$, indicating that YbAuCu$_4$ is situated close to the quantum critical point [4, 19]. The temperature dependences of $1/T_1 T$ at high temperatures under several magnetic fields follow the Curie-Weiss law and take a broad maximum at the characteristic temperature $T_v$. Wada et al. claimed that the crossover valence transition occurs at $T_v$, which is stabilized by the application of external magnetic field [18]. The temperature dependence of the nuclear quadrupole frequency $\nu_Q$ decreases significantly below $T_v \simeq 10$ K at $\mu_0 H = 7$ T, and Wada et al. suggested the expansion of the unit cell volume through $T_v$ with decreasing temperature. In the present study, we performed precise thermal expansion and magnetostriction measurements of polycrystalline samples in the temperature range down to 1.4 K under magnetic fields of up to 7 T in order to study the lattice dynamics due to the crossover valence
Figure 2: Temperature dependences of (a) the thermal expansion coefficient $\alpha$ and (b) the thermal expansion $\Delta l/l$ of YbAuCu$_4$ and LuAuCu$_4$.

1.1 Experimental Procedure

Polycrystalline YbAuCu$_4$ samples were prepared by slow-cooling method as in the previous studies [12, 14]. Starting materials in stoichiometric ratios of Yb: Au: Cu = 1:1:4 were placed in an alumina crucible, and the crucible was sealed into a tantalum (Ta) crucible by the tetra-arc furnace with Ar atmosphere. The Ta crucible was sealed into a quartz tube with Ar atmosphere, which was adjusted to become 1 bar at 1400 °C. The quartz tube was heated to 1400 °C in 12 hours and kept for 1 hour, and then slowly cooled to 1000 °C in 5 hours. Finally, the furnace was turned off. A similar procedure was applied for preparation of LuAuCu$_4$ polycrystals. X-ray powder diffraction analyses provided no evidence of impurity phases both in YbAuCu$_4$ and LuAuCu$_4$.

The electrical resistivity was measured by the ordinary four-probe AC method. The specific heat was measured by the quasi-adiabatic heat-pulse method in the temperature range between 1.4 and 60 K. The thermal expansion and magnetostriction were measured by the three-terminal capacitance method in the temperature range between 1.4 and 300 K and under magnetic fields of up to 7 T.

1.2 Experimental Results and Discussion

Figures 1(a) and 1(b) show the temperature dependences of the specific heat $C$ under several magnetic fields and the electrical resistivity $\rho$ at $\mu_0 H = 0$ of YbAuCu$_4$, respectively. $\rho$ shows pronounced temperature dependence with two minima at $\sim 100$ and $\sim 5$ K and maxima at $\sim 20$ and $\sim 1.1$ K, which is consistent with the previous results [12, 13]. In addition, the present resistivity at around 1 K, $\rho \simeq 24 \, \mu\Omega \cdot \text{cm}$, is almost the same value with the previous results [13].

The temperature dependence of $C$ at $\mu_0 H = 0$ shows a minimum at approximately 3.5 K and increases with decreasing temperature. When the magnetic field of 2 T is applied, a broad maximum of $C$ appears at approximately 2 K. This broad peak shifts to higher temperatures.
with increasing magnetic field, reaching about 5 K at 7 T. These features of C under magnetic fields have already been observed by Bauer et al., and analyzed on the basis of the crystalline electric field scheme [16, 13]. The broad peak was well explained by the Schottky anomaly due to the Zeeman splitting of the Γ7 ground-state doublet. The temperature dependences of ρ and C of the present polycrystalline samples verify the bulk properties of YbAuCu4.

Temperature dependences of the thermal expansion coefficient α and thermal expansion (relative length change) Δℓ/ℓ of YbAuCu4 and the reference compound LuAuCu4 are shown in Fig. 2. The temperature dependences of α of YbAuCu4 and LuAuCu4 almost coincide with each other except for low temperatures below about 50 K. α of YbAuCu4 is slightly larger than that of LuAuCu4 in this temperature range, indicating magnetic contributions to α of YbAuCu4. Δℓ/ℓ of both compounds decreases approximately linearly from the room temperature and gradually approaches to zero with decreasing temperature. In our previous investigations, negative thermal expansions were observed at low temperatures in some Yb-based heavy-fermion compounds such as YbCu2Si2 [20] and YbT2Zn20(T:Co, Rh, Ir) [21]. The temperature dependence of Δℓ/ℓ shows a minimum at approximately the Kondo temperature TK and increases slightly with decreasing temperature. The negative thermal expansion of YbT2Zn20(T:Co, Rh, Ir) was discussed in relation to the valence change of Yb ions against temperature [21]. The absence of negative thermal expansion in YbAuCu4 might be consistent with the fact that the Kondo temperature is quite low in this compound, namely TK = 1.65 K [13]. Note that the temperature dependences of α of YbAuCu4 and LuAuCu4 were already measured using strain gauges by Hauser et al. [22]. The present α of LuAuCu4 is almost the same with the previous result. However, the previous α of YbAuCu4 shows a minimum at approximately 20 K and increases with decreasing temperature, which is somewhat different from the present result.

Figures 3(a) and 3(b) depict the temperature dependences of α on a logarithmic temperature scale and Δℓ/ℓ on a linear temperature scale of YbAuCu4 under several selected magnetic fields, respectively. In the present experiment, the length change of the sample parallel to the applied magnetic field was measured, namely in the longitudinal configuration. The temperature dependences of Δℓ/ℓ in Fig. 3(b) under magnetic fields are plotted by normalizing the values of
Figure 4: (a) Longitudinal magnetostriction $\varepsilon_{\parallel}$ curves at several constant temperatures of YbAuCu$_4$ and (b) magnetic field dependences of $\langle O^{0}_{2} \rangle$ calculated on the basis of the CEF model. Broken lines in (a) are that same with the calculated lines at corresponding temperatures in (b).

$\Delta \ell/\ell$ at 30 K to the magnetostriction curve $\varepsilon_{\parallel} (=\Delta \ell/\ell)$ at 30 K which will be shown later. At $\mu_0 H = 0$, $\alpha$ shows a minimum at approximately 5 K and increases slightly with decreasing temperature. When the magnetic field is increased, the increase of $\alpha$ at low temperatures becomes large, and a broad peak appears at approximately 2 K at 2.0 T. The broad peak shifts to higher temperatures with increasing magnetic field: $\sim 4$ K at 3.0 T, $\sim 5$ K at 5.0 and 7.0 T. In addition, another negative broad peak can be seen at 5.0 T below 2 K. It is well known that the thermal expansion coefficient $\alpha$ can be connected with the corresponding specific heat $C$ through the thermodynamical Grüneisen relation. Therefore, the observed broad peaks in $\alpha$ will correspond to those in $C$, as shown in Fig. 1, and might be due to the crystalline electric field effect.

The corresponding temperature dependences of $\Delta \ell/\ell$ are plotted in Fig. 3(b). $\Delta \ell/\ell$ decreases almost linearly at high temperatures and gradually approaches to zero at $\mu_0 H = 0$. On the other hand, $\Delta \ell/\ell$ under magnetic fields shows another marked decrease in the temperature range below approximately 10 K. For example, $\Delta \ell/\ell$ at 7.0 T shows a shoulderlike feature at approximately 10 K and decreases rapidly for further decreasing temperature. As mentioned in Section 1, Wada et al. observed a rapid decrease of the nuclear quadrupole frequency $\nu_Q$ of YbAuCu$_4$ below $T_v = 10$ K at 7.0 T for example, and the authors claimed that the crossover valence transition takes place at around $T_v$ [18]. In addition, they pointed out that the significant decrease of $\nu_Q$ observed below $T_v$ provides evidence for the expansion of unit-cell volume ($\propto 1/\nu_Q$). In the present experiments, the linear thermal expansion $\Delta \ell/\ell$ under 7.0 T decreases more rapidly below about 10 K and is leveling off below about 2 K, as shown in Fig. 3(b). These features might suggest a contraction of the unit-cell volume. However, to discuss the temperature dependence of the unit-cell volume, it is necessary to measure $\Delta \ell/\ell$ perpendicular to the applied magnetic field, because the large anisotropic magnetostriction has been reported in YbAuCu$_4$ [23].

Figure 4(a) shows the longitudinal magnetostriction $\varepsilon_{\parallel}$ along the applied magnetic field at
several constant temperatures. As shown in the figure, negative magnetostrictions were observed at all the measured temperatures below 50 K, namely the sample length parallel to the magnetic field contracts with increasing magnetic field. $\varepsilon_\parallel$ above 20 K decreases as $H^2$. On the other hand, $\varepsilon_\parallel$ changes as $H^2$ at low magnetic fields as well but deviates from the $H^2$-dependence at high magnetic fields at lower temperatures. In particular, $\varepsilon_\parallel$ at 1.4 K starts decreasing as $H^2$ below about 1 T, shows a shoulderlike behavior at around 2 T and decreases further at higher magnetic fields. These characteristic features of magnetostriction are also observed in the temperature dependence of thermal expansion $\Delta \ell/\ell$ shown in Fig. 3(b), indicating a peculiar decrease of $\Delta \ell/\ell$ at 1.4 K. Since the antiferromagnetic ordering temperature $T_N \simeq 0.6$ K is close to the experimental temperature of 1.4 K, the antiferromagnetic correlation might be the cause of these features, and further experiments at lower temperatures are necessary to elucidate the origin.

To analyze the observed $\varepsilon_\parallel$ curves of YbAuCu$_4$, we simply calculated the magnetic field dependence of $\langle O_L^0 \rangle$ on the basis of the CEF scheme observed by neutron scattering experiments [16]. The CEF Hamiltonian for the cubic site symmetry is given by [24]

$$\mathcal{H}_{\text{CEF}}^{\text{cubic}} = B_4 \langle O_4^0 + 5O_4^1 \rangle + B_6 \langle O_6^0 - 21O_6^1 \rangle$$

$$W \left[ x \left( \frac{O_4^0 + 5O_4^1}{F(4)} \right) + (1 - |x|) \left( \frac{O_6^0 - 21O_6^1}{F(6)} \right) \right]$$

where $B_l$ are the CEF parameters, $O_l^m$ are the Stevens operators [25, 26], and $F(4) = 60$ and $F(6) = 1260$ for the Yb$^{3+}$ ion with $J = 7/2$. $W = -2.611$ K and $x = -0.945$ reproduce CEF excitation energies at 45 K for $\Gamma_8$ and 80 K for $\Gamma_6$ [16]. We calculated eigenvalues and eigenfunctions in magnetic fields using the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{CEF}}^{\text{cubic}} - g_J \mu_B J \cdot H,$$

where $g_J$ is the Landé $g$-factor and $J$ is a component of the angular momentum. The magnetostriction is in proportion to the thermal average of $O_L^0 = \{ J^2 - J(J + 1)/3 \}/2$, namely $\varepsilon_\parallel \propto \langle O_L^0 \rangle$ [27], and we calculated the magnetic field dependences of $\langle O_L^0 \rangle$ using eigenvalues and eigenfunctions in magnetic fields at several temperatures, as shown in Fig. 4(b). The calculated curves are normalized to the experimental results below about 2 T at low temperatures, as indicated by broken lines in Fig. 4(a). Although somewhat large disagreements are observed at high magnetic fields at low temperatures, the present magnetostriction results can be sketched by the evolution of $\langle O_L^0 \rangle$ under magnetic fields.

### 1.3 Summary

We performed precise thermal expansion and magnetostriction measurements of YbAuCu$_4$ in order to examine the crossover valence transition which was proposed by NMR measurements. The temperature dependence of the thermal expansion coefficient $\alpha$ at $\mu_0 H = 0$ of YbAuCu$_4$ is almost the same with that of the reference compound LuAuCu$_4$ except for the small difference below about 50 K. This might be due to the presence of magnetic contribution, presumably crystalline electric field effects, in YbAuCu$_4$. Under magnetic fields, a broad peak is observed in $\alpha$ at low temperatures, which is similar to the broad peak observed in C under magnetic fields. Corresponding temperature dependence of $\Delta \ell/\ell$ parallel to the magnetic field of 7.0 T shows a large and marked decrease below about 10 K, indicating a large contraction of the sample length with decreasing temperature. The longitudinal magnetostriction $\varepsilon_\parallel$ is negative below 50 K, implying that the sample length along the magnetic field contracts by applying magnetic...
fields. The observed $\varepsilon_\parallel$ is compared with the magnetic field variation of $\langle O_2^0 \rangle$ calculated on the basis of the proposed CEF scheme.

References

[1] Y. Onuki and R. Settai, Low Temp. Phys. 38, 89 (2012).
[2] Y. Onuki, R. Settai, T. Takeuchi, K. Sugiyama, F. Honda, Y. Haga, E. Yamamoto, T. D. Matsuda, N. Tateiwa, D. Aoki, I. Sheikin, H. Harima, and H. Yamagami, J. Phys. Soc. Jpn. 81, SB001 (2012).
[3] S. Doniach, *Valence Instabilities and Related Narrow Band Phenomena*, ed. R. D. Parks (Plenum, New York, 1977) p. 169.
[4] P. Gegenwart, J. Custers, C. Geibel, K. Neumaier, T. Tayama, K. Tenya, O. Trovarelli, and F. Steglich, Phys. Rev. Lett. 89, 056402 (2002).
[5] 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 (2008).
[6] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism*, (Springer, Berlin, 1985).
[7] J. A. Hertz, Phys. Rev. B14, 1165 (1976).
[8] A. J. Millis, Phys. Rev. B48, 7183 (1993).
[9] S. Watanabe and K. Miyake, Phys. Rev. Lett. 105, 186403 (2010).
[10] S. Watanabe, A. Tsuruta, K. Miyake, and J. Flouquet, J. Phys. Soc. Jpn. 78, 104706 (2009).
[11] I Felner, I Nowik, Phys. Rev. B33, 617 (1986).
[12] C. Rossel, K. N. Yang, M. B. Maple, Z. Fisk, E. Zirngiebl, and J. D. Thompson, Phys. Rev. B35, 1914 (1987).
[13] E. Bauer, E. Gratz, R. Hauser, La Tuan, A. Galatamu, A. Kottar, H. Michor, W. Perhold, G. Hilscher, T. Kagayama, G. Oomi, N. Ichimiya, and S. Endo, Phys. Rev. B50, 9300 (1994).
[14] J. L. Sarrao, C. D. Immer, Z. Fisk, C. H. Booth, E. Figueroa, J. M. Lawrence, R. Modler, A. L. Cornelius, M. F. Hundley, G. H. Kwei, J. D. Thompson, and F. Bridges, Phys. Rev. B59, 6855 (1999).
[15] E. Bauer, P. Fischer, F. Marabelli, M. Ellerby, K. A. McEwen, B. Roessli, and M. T. Fernades-Dias, Physica B234-236, 676 (1997).
[16] A. Severing, A. P. Murani, J. D. Thompson, Z. Fisk, and C. -K, Loong, Phys. Rev. B41, 1739 (1990).
[17] A. Yamamoto, S. Wada, and J. L. Sarrao, J. Phys. Soc. Jpn. 76, 063709 (2007).
[18] S. Wada, A. Yamamoto, K. Ishida, and J. L. Sarrao, J Phys.: Condens. Matter 20, 175201 (2008).
[19] S. Paschen, T. Lüthmann, S. Wirth, P. Gegenwart, O. Trovarelli, C. Geibel, F. Steglich, P. Coleman, and Q. Si, Nature 432, 881 (2004).
[20] N. D. Dung, T. D. Matsuda, Y. Haga, S. Ikeda, E. Yamamoto, T. Ishikura, T. Endo, S. Matsuoka, Y. Aoki, H. Sato, T. Takeuchi, R. Settai, H. Harima, and Y. Onuki, J. Phys. Soc. Jpn. 78, 084711 (2009).
[21] T. Takeuchi, S. Yoshiuchi, Y. Hirose, F. Honda, R. Settai, and Yoshichika Onuki, JPS Conf. Proc. 3, 011017 (2014).
[22] R. Hauser, T. Ishii, Y. Uwatoko, G. Oomi, E. Bauer, and E. Gratz, J. Magn. Magn. Mater. 157-158, 679 (1996).
[23] A. Yu Sokolov, H. Nakamura, and M. Shiga, J. Phys.: Condens. Matter 11, 6463 (1999).
[24] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).
[25] K. W. H. Stevens: Proc. Phys. Soc., Sect. A 65, 209 (1952).
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[26] M. T. Hutchings: in Solid State Physics: Advances in Research and Applications, eds. F. Seitz and B. Turnbull (Academic, New York, 1965) Vol. 16, p. 227.

[27] M. Sera, S. Itabashi, and S. Kunii, J. Phys. Soc. Jpn. 66, 548 (1997).