Anomalous Enhancement of Seebeck Coefficient in Pr-Based 1-2-20 System with Non-Kramers Doublet Ground States

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Abstract. Low-temperature Seebeck coefficient S/T measurements have been performed on Pr-based 1-2-20 system, $\mathrm{Pr}Tr_2X_{20}$ (Tr = Ti, Ta, V, Ir, X = Al, Zn) with non-Kramers doublet ground states. For $\mathrm{Pr}Tr_2X_{20}$ with X = Al, we find a large S/T, which amounts to those of heavy fermion metals. By contrast, S/T for $\mathrm{PrIr_2Zn_{20}}$ is found to be considerably small as the same order of magnitude as those of ordinary metals, despite the commonly enhanced Sommerfeld coefficient γ throughout the system. A satisfactory of the quasi-universal relation between S/T and γ as well as the Kadowaki-Woods relation demonstrates that the mass enhancement is realized in $\mathrm{Pr}Tr_2\mathrm{Al}_{20}$ due to the hybridization between f-electrons and the conduction electrons. We also find that the small S/T of $\mathrm{PrIr_2Zn_{20}}$ is enhanced at low temperatures under the fields on the verge of quadrupole ordered phase, and in the same regime, the electrical resistivity follows the quadratic temperature dependence with a steep slope as a characteristic of Fermi liquid. The results imply an emergence of a nontrivial coherent state with sizable mass enhancement associated with the quadrupole degree of freedom.

1. Introduction

In f-electron system with an odd number as in Ce-based compounds, large entropy due to Kramers doublet is released by quenching magnetic f-moment through hybridization with conduction electrons via the Kondo effect or by polarizing the f-moments via the RKKY interaction. In the former, strong electronic correlation is renormalized into effective quasiparticle mass, and eventually the Fermi liquid state with sizable mass enhancement, called heavy fermion state, is formed at the ground state. The mass enhancement is usually detected as a large Sommerfeld coefficient γ and a large T^2 term A of the electrical resistivity due to a large density of states at the Fermi energy induced by electronic correlation effect. Consequently, this leads to the Kadowaki-Woods ratio [1] relating these two quantities (A/γ^2) because strong renormalization effects in γ and A cancel each other out. Therefore, the Kadowaki-Woods ratio is a robust consequence of the Fermi liquid and is useful to verify whether these quantities come from the mass enhancement. It should be noted, however, that localized contribution to the

specific heat and sensitivity to impurities of the electrical resistivity are sometimes problematic in detecting purely electronic signature of correlation.

Recently, it has been recognized that the Seebeck coefficient S is a powerful probe of the mass enhancement, and would be complementary to γ and A by virtue of its sensitivity to itinerant electronic excitation. In a Boltzmann picture,, the Seebeck coefficient is determined by the logarithmic energy derivative of the electrical conductivity σ [2],

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\left[\frac{\partial \ln\sigma(\varepsilon)}{\partial\varepsilon}\right]_{\varepsilon_F}. \tag{1}$$

This can be rewritten as

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\left[\frac{\partial \ln\tau(\varepsilon)}{\partial\varepsilon} + \frac{\partial \ln N(\varepsilon)}{\partial\varepsilon}\right]_{\varepsilon_F}, \tag{2}$$

with $\tau(\varepsilon)$ denoting the relaxation time of the conduction electrons, and $N(\varepsilon)$ denoting the electronic density of states (DOS) at the Fermi level ε_F. Therefore, one can expect the enormously enhanced Seebeck coefficient, if the DOS is largely asymmetric at ε_F. This may be realized in the heavy fermion systems at low temperatures in which a sharp Kondo peak in the DOS near ε_F is caused by the hybridization between the f-electron and conduction electrons. In fact, a number of the heavy fermion compounds exhibits the large Seebeck coefficient up to three order of magnitude higher than the one of simple metals [3]. Furthermore, in the case of a free electron gas and in the zero-temperature limit, equation (2) can be further rewritten as

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\frac{N(\varepsilon_F)}{n}\left(1 + \frac{2\zeta}{3}\right), \tag{3}$$

where n is the carrier concentration and ζ is the exponent of energy dependence of the scattering time, $\tau(\varepsilon) = \tau_0\varepsilon^\zeta$ [3]. In this simplest case, the Seebeck coefficient is linear as a function of temperature and is directly proportional to the density of states at the Fermi energy as the same as the specific heat, and thus, S and γ are expected to be interrelated. Indeed, it has been demonstrated that a wide range of materials exhibits a remarkable correlation and a dimensionless ratio $q = (S/T\gamma)\times N_{Av}e$ (N_{Av}: the Avogadro number) linking these two quantities is order of unity in spite of the over-simplification [3]. Therefore, the Seebeck coefficient provides another semi-universal ratio for strongly correlated electron systems in addition to the Kadowaki-Woods ratio, enabling alternative confirmation of the mass renormalization effect in a given system.

In the paper, we adopted this technique to clarify possible mass enhancement in Pr-based 1-2-20 system with non-Kramers doublet ground states, in which a nonmagnetic analog of the Kondo effect is though to be realized.

2. Pr-based 1-2-20 system
The Kondo effect using a magnetic dipole moment is well established both experimentally and theoretically, and it has provided several intriguing phenomena such as heavy fermion state, unconventional superconductivity, and quantum criticality. On the other hand, it remains elusive whether nonmagnetic Kondo effect, so called quadrupolar Kondo effect is possible based on hybridization between a quadrupole moment of non-Kramers Γ_3 doublet and conduction electrons, despite the theoretical proposal predicting non-Fermi liquid behaviors due to overscreening of localized electron by conduction electrons [4,5]. One of the reason preventing experimental investigation of such intriguing possibility is due to a lack of suitable systems with well-defined non-Kramers doublet.

A recent discovered cubic Pr-based 1-2-20 system, $\mathrm{Pr}Tr_2X_{20}$ (Tr: transition metal, X = Al, Zn), offers a rare opportunity to unveil interplay between quadrupole moments and conduction electrons [6-9]. This is because $4f$-electrons in the Pr ions have a clear crystalline electric field (CEF) splitting with the non-Kramers Γ_3 doublet ground state where quadrupole degree of freedom is active [10,11]. In addition, a large coordination number of ligand X ions surrounding the Pr ion increases hybridization strength to conduction electrons. $\mathrm{Pr}Tr_2X_{20}$ undergoes quadrupole order at certain temperatures T_Q [7-9] as shown in Table 1. In $\mathrm{PrTi_2Al_{20}}$, $\mathrm{PrV_2Al_{20}}$, and $\mathrm{PrIr_2Zn_{20}}$, superconductivity coexists with the quadrupole order [7,12,13]. Strikingly, the system exhibits intriguing properties, for example $\rho \propto \sqrt{T}$ for $\mathrm{PrV_2Al_{20}}$ and $\mathrm{PrIr_2Zn_{20}}$, at low temperatures above T_Q [8,14]. Moreover, the specific heat is largely enhanced up to the values comparable with those of the heavy fermion metals [7-9], and that is interpreted as observing the mass enhancement due to the hybridization between the quadrupole moments and conduction electrons. However, we should be careful here because the specific heat does not always measure itinerant electronic excitation only, and so that the above interpretation is not conclusive.

Here, we carried out a systematic study of the low-temperature Seebeck coefficient and electrical resistivity on Pr-based 1-2-20 system, $\mathrm{Pr}Tr_2X_{20}$ (Tr = Ti, Ta, V, Ir, X = Al, Zn), and examined the putative mass enhancement. Since the Seebeck coefficient only measures itinerant excitations that is an advantage of this quantity over the specific heat, it would be a good probe of the renormalized effective mass due to the electronic correlation.

3. Experiments

Single crystals were prepared by a Al and Zn self-flux method for $\mathrm{Pr}Tr_2\mathrm{Al_{20}}$ [8,9] and $\mathrm{PrIr_2Zn_{20}}$ [7], respectively. Contact were made by a spot welding technique, and were used to measure both Seebeck coefficient and electrical resistivity in a dilution refrigerator down to 40 mK. The Seebeck coefficient S was measured by a standard two-thermometers-one-heater steady-state method. The electrical resistivity ρ was measured by a four-contacts method. The electrical and heat current were injected along the [010] and [110] directions for $\mathrm{PrIr_2Zn_{20}}$ and $\mathrm{Pr}Tr_2\mathrm{Al_{20}}$, respectively. The magnetic field H was applied along the [111] direction for $\mathrm{PrTi_2Al_{20}}$. For $\mathrm{PrIr_2Zn_{20}}$, the magnetic field was parallel to the [100] and [010] directions for the Seebeck coefficient and electrical resistivity measurements, respectively. The residual resistivity ratio (RRR) reaches up to 90, 6, 6, and 870 for $\mathrm{PrTi_2Al_{20}}$, $\mathrm{PrTa_2Al_{20}}$, $\mathrm{PrV_2Al_{20}}$, and $\mathrm{PrIr_2Zn_{20}}$, respectively.

4. Results and Discussions

Figure 1 shows the temperature dependence of the Seebeck coefficient divided by temperature S/T for $\mathrm{PrTi_2Al_{20}}$, $\mathrm{PrTa_2Al_{20}}$, $\mathrm{PrV_2Al_{20}}$, and $\mathrm{PrIr_2Zn_{20}}$. Here, a weak field of $\mu_0 H = 6$ mT and 1 mT greater than the upper critical field is applied for $\mathrm{PrTi_2Al_{20}}$ and $\mathrm{PrIr_2Zn_{20}}$, respectively, to eliminate the superconductivity. First of all, we emphasize that magnitude of S/T for $\mathrm{Pr}Tr_2X_{20}$ with X = Al is large, which is comparable to those of heavy fermion metals [3], even above the quadrupolar ordering temperatures T_Q where the quadrupole degree of freedom of the non-Kramers Γ_3 doublet is dominant because of a large energy splitting $\sim$ 30-50 K to the first excited state [10,11]. By further decreasing the temperature, $|S/T|$ continues to increase, but shows a tendency to saturate at low temperatures as a hallmark of the Fermi liquid. At the lowest temperature, S/T reaches up to -3 $\mu\mathrm{V/K}^2$, -10 $\mu\mathrm{V/K}^2$, and -22 $\mu\mathrm{V/K}^2$ for $\mathrm{PrTi_2Al_{20}}$, $\mathrm{PrTa_2Al_{20}}$, and $\mathrm{PrV_2Al_{20}}$, respectively. Here, it is important to note that the order of magnitude of S/T is the same with the one of the Sommerfeld coefficient γ as listed in Table 1. In contrast to the enhanced S/T for the case with X = Al, S/T for $\mathrm{PrIr_2Zn_{20}}$ is almost temperature-independent in the measured temperature range, and its magnitude (~ 0.03 $\mu\mathrm{V/K}^2$) is considerably small as the same order of magnitude as those of ordinary metals [3]. This result is somewhat surprising because γ is commonly enhanced throughout the systems
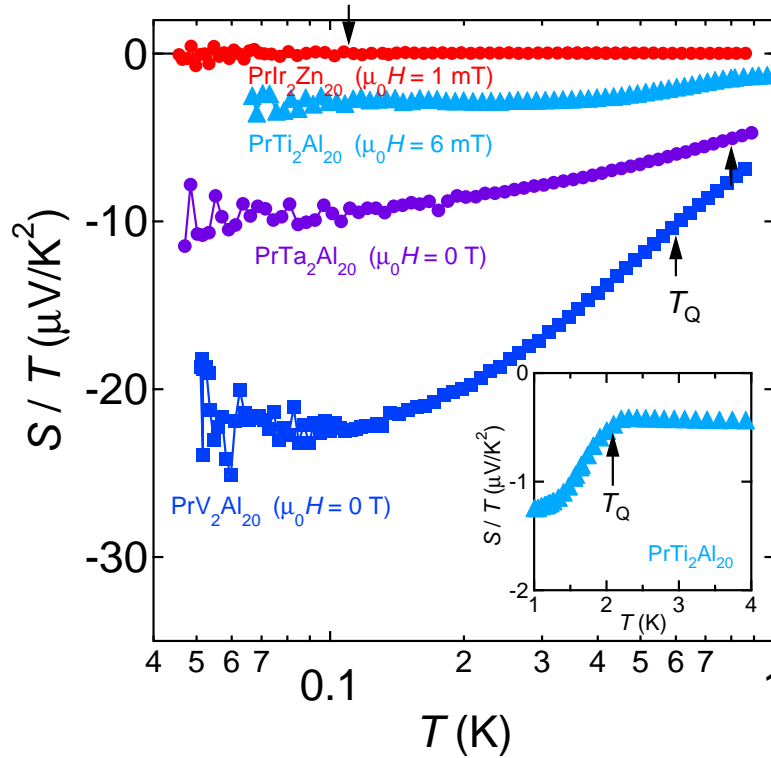
Figure 1. Temperature dependence of the Seebeck coefficient divided by temperature S/T for $PrTi_2Al_{20}$, $PrTa_2Al_{20}$, PrV_2Al_{20}, and $PrIr_2Zn_{20}$ on a semi-logarithmic scale. A weak field of $\mu_0 H = 6$ mT and 1 mT greater than the upper critical fields is applied for $PrTi_2Al_{20}$ and $PrIr_2Zn_{20}$, respectively, to eliminate the superconductivity. Inset: S/T vs. T plot above 1 K for $PrTi_2Al_{20}$. Arrows indicate the quadrupolar ordering temperatures T_Q.

irrespective of X ions up to two or three order of magnitude higher than the one of simple metals (Table 1). As we mentioned above, the Seebeck coefficient can be a good measure of the density of state (DOS) of itinerant electrons at the Fermi level $N(\varepsilon_F)$ in some cases at low-enough temperature [3]. Thus, the large S/T observed here in $PrTr_2Al_{20}$ suggests strong renormalization effect that enhances the DOS, but such effect seems to be weak in $PrIr_2Zn_{20}$.

This argument is further supported by a S/T vs. γ plot as shown in Fig. 2, which demonstrates that S/T and γ for various materials including not only simple metals but also heavy fermion metals obey a universal relation in a logarithmic accuracy [3] . This is based on the fact that γ is proportional to $N(\varepsilon_F)$ and S/T may also be approximated as $S/T \propto N(\varepsilon_F)$ in the simplest case [3]. From the plot, it is clearly seen that the semi-universal relation is valid for the case with $X =$ Al, but is apparently failed for $PrIr_2Zn_{20}$. Therefore, the renormalization effect is responsible for enhancement of S/T and γ for $PrTr_2X_{20}$ with $X =$ Al. On the other hand, the effect is significantly weak in $PrIr_2Zn_{20}$, and the large γ is not likely to be due to a contribution from itinerant electronic excitation. We note that weak mass renormalization in $PrIr_2Zn_{20}$ is also indicated by the de Haas-van Alphen (dHvA) experiments with small cyclotron effective mass $\sim 1\ m_0$ [15].
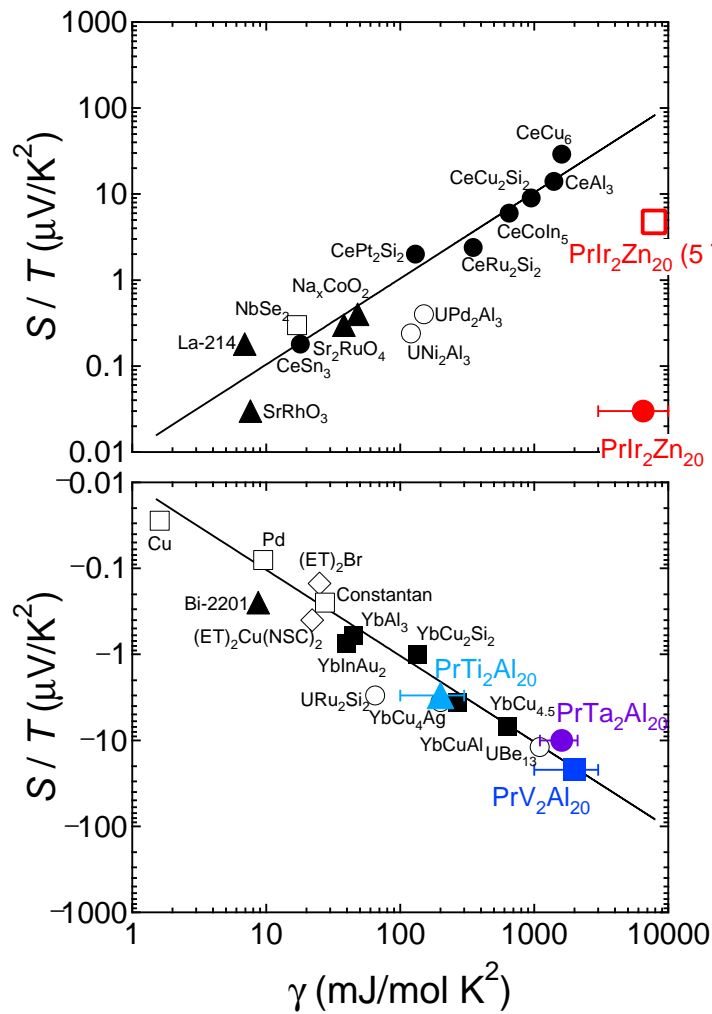
Figure 2. Relation between the Seebeck coefficient S/T and the Sommerfeld coefficient γ for $PrTi_2Al_{20}$, $PrTa_2Al_{20}$, PrV_2Al_{20}, and $PrIr_2Zn_{20}$. Data for other compounds are taken from the figure in Ref. [3]. Two solid lines represent $q = \pm\,1$.

Table 1. A comparison of physical parameters in $PrTi_2Al_{20}$, $PrTa_2Al_{20}$, PrV_2Al_{20}, and $PrIr_2Zn_{20}$. Zero-field values of $|S/T|$ and A coefficient for $PrTi_2Al_{20}$ and $PrIr_2Zn_{20}$ are obtained under a weak field of $\mu_0 H = 6$ mT and 1 mT, respectively.

| | $PrTi_2Al_{20}$ | $PrTa_2Al_{20}$ | PrV_2Al_{20} | $PrIr_2Zn_{20}$ | |
	0 T	0 T	0 T	0 T	5 T
T_Q (K)	2.0	0.8	0.6	0.11	-
$|S/T|$ (μV/K^2)	3	10	22	0.03	3
γ (J/molK^2)	0.1-0.3[8]	1.1-2.1[9]	1-3[8]	3-10[7]	7.8[14]
$|q|$	1.0-2.9	0.5-0.9	0.7-2.1	0.001-0.003	0.4
A ($\mu\Omega$cm/K^2)	0.15	6.0	19.4	-	10.5
A/γ^2 (a$_0$)	0.17-1.5	0.14-0.5	0.22-1.9	-	0.017

Figure 3. Electrical resistivity ρ as a function of T^2 for (a) PrTi$_2$Al$_{20}$ at $\mu_0 H = 6$ mT, (b) PrTa$_2$Al$_{20}$ at $\mu_0 H = 0$ T, (c) PrV$_2$Al$_{20}$ at $\mu_0 H = 0$ T, and (d) PrIr$_2$Zn$_{20}$ at $\mu_0 H = 1$ mT and 5 T.

Alternative confirmation of the strong renormalization effect in PrTr_2Al$_{20}$ is given by the electrical resistivity. Figures 3(a)-(d) show the temperature dependence of the electrical resistivity ρ as a function of T^2 for PrTi$_2$Al$_{20}$, PrTa$_2$Al$_{20}$, PrV$_2$Al$_{20}$, and PrIr$_2$Zn$_{20}$. Again, a weak field greater than the upper critical field is applied for PrTi$_2$Al$_{20}$ and PrIr$_2$Zn$_{20}$. For the case of $X =$ Al, ρ follows T^2 dependence at low temperatures as a characteristic signature of Fermi liquid. Importantly, order of evaluated T^2 term, A coefficient with $\rho(T) = \rho_0 + AT^2$, is also the same as those of S/T and γ, as shown in Table 1. Moreover, the Kadowaki-Woods ratio A/γ^2 is close to the universal value $a_0 = 1.0 \times 10^{-5}$ $\mu\Omega$cm(molK^2/mJ) (Table 1) [1], and thus the Kadowaki-Woods relation is valid in PrTr_2Al$_{20}$ up to logarithmic accuracy as shown in Fig. 4. On the contrary, the temperature dependence of ρ for PrIr$_2$Zn$_{20}$ is very weak at low temperatures, so that an estimation of the T^2 term is far from reliable. We infer that this may be due to the weak renormalization effect in PrIr$_2$Zn$_{20}$ as indicated by the small S/T as well as the small effective mass determined by the dHvA experiments [15]. The fact that three distinct, but mutually correlated quantities S/T, γ, and A coefficient are largely enhanced reveals a realization of the strong mass enhancement in PrTi$_2$Al$_{20}$, PrTa$_2$Al$_{20}$, and PrV$_2$Al$_{20}$ due to the hybridization between f-electrons and conduction electrons. More precisely, given that

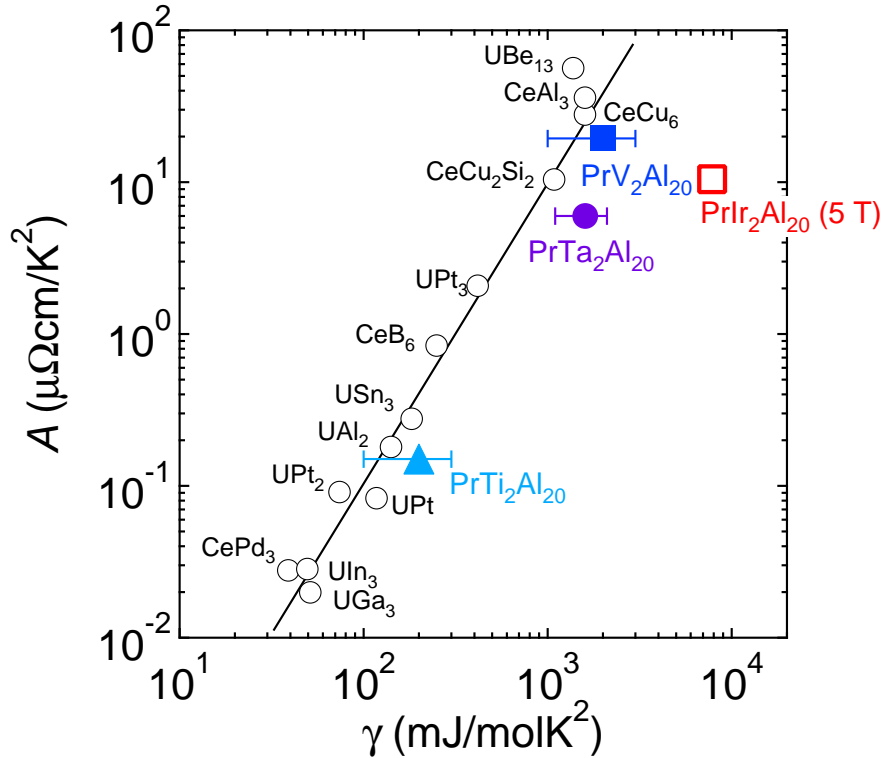**Figure 4.** Kadowaki-Woods plot of the T^2 coefficient of electrical resistivity A vs. the Sommerfeld coefficient γ for $PrTi_2Al_{20}$, $PrTa_2Al_{20}$, PrV_2Al_{20}, and $PrIr_2Zn_{20}$. Data for other compounds are taken from the figure in Ref. [1].

the system has the Γ_3 quadrupole degree of freedom, one may speculate an interplay between the quadrupole moments and the conduction electrons as a source of the enhancement.

A marked difference in the hybridization strength between $X = Al$ and Zn compounds may be due to a different character of electrons of the ligand ions, namely d and s-electrons in the Zn and Al ions, respectively. The difference in the hybridization effect between $PrTi_2Al_{20}$ and PrV_2Al_{20} appeared in the magnitude of S/T, γ, and A is due to the additional $3d$ conduction electrons and the smaller unit cell volume in the latter. On the other hand, it is not straightforward to understand the less pronounced difference between $PrTa_2Al_{20}$ and PrV_2Al_{20}, but it may attribute to a difference in d-electron number rather than a volume expansion effect. This is because the replacement of V by Ti or Ta expands the unit cell volume by a similar amount up to a few % [9,16], while it gives rise to the reduction of S/T by a factor of ~ 7 and ~ 2, respectively.

Having established the weak hybridization in $PrIr_2Zn_{20}$, we now turn to observation of a dramatic enhancement of signatures of electronic correlation on the verge of quadrupole ordered phase. Figure 5 shows the temperature dependence of S/T for $PrIr_2Zn_{20}$ at $\mu_0 H = 5$ T together with S/T at $\mu_0 H = 1$ mT, the same data with the one in Fig. 1. At $\mu_0 H = 5$ T around where the quadrupole ordering is collapsed when the magnetic field is applied along the [100] direction [17,18], S/T exhibits a striking increase with decreasing the temperature and form a peak around 80 mK with a peak value ~ 4.5 $\mu V/K^2$ that is more than 100 times larger than the value at 1 mT. Interestingly, the peak value is large as much as the one expected from large γ through the semi-universal relation between S/T and γ, as displayed in Fig. 2. It is also interesting to note
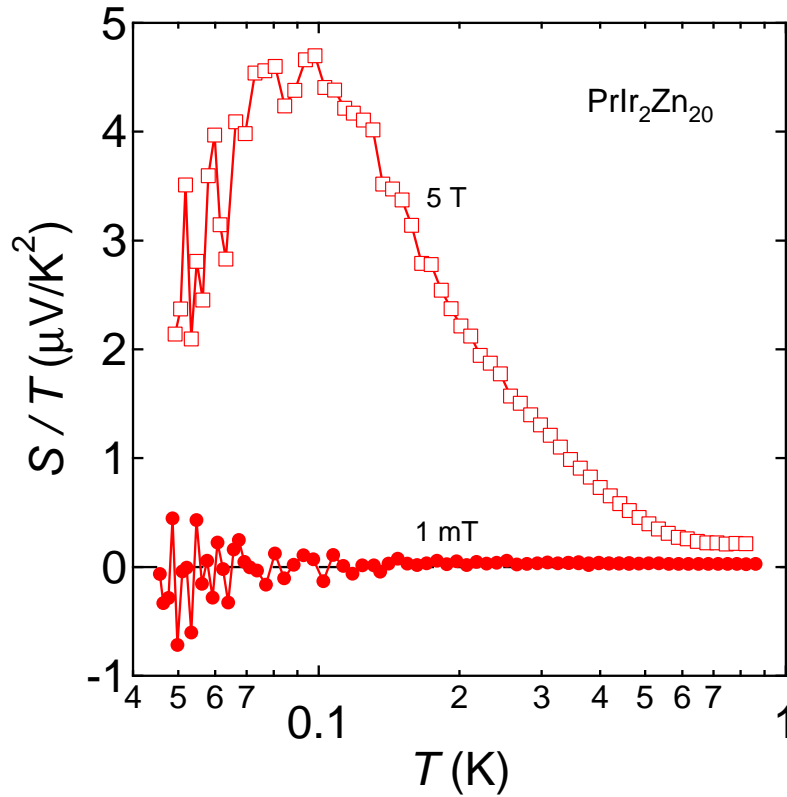
Figure 5. Temperature dependence of the Seebeck coefficient divided by temperature S/T for PrIr$_2$Zn$_{20}$ at $\mu_0 H = 1$ mT and 5 T.

that, under the same field, the resistivity shows the quadratic temperature dependence at low temperatures with a steep slope (Fig. 3(a)). An extracted A coefficient is also large as expected from the large γ, and satisfies the Kadowaki-Woods relation as shown in Fig. 4. These findings implies that when the quadrupolar ordering is collapsed, a non-trivial many-body state with the sizable mass enhancement associated with the quadrupole degree of freedom is developed.

5. Summary
Our systematic study on the low-temperature Seebeck coefficient S/T of Pr-based 1-2-20 system, PrTr_2X_{20} (Tr = Ti, Ta, V, Ir, X = Al, Zn), reveals the anomalous enhancement of S/T for PrTr_2X_{20} with X = Al, in which S/T reaches up to the values observed in the heavy fermion systems. Simultaneous verification of the universal ratios for the strongly correlated electron systems, namely the dimensionless ratio of S/T and γ, and the Kadowaki-Woods ratio, unambiguously indicates the realization of the mass enhancement in PrTr_2Al$_{20}$ due to the strong hybridization between f-electrons and the conduction electrons. By contrast, S/T of PrIr$_2$Zn$_{20}$ is found to be extremely small, revealing the marked difference in the hybridization strength between X = Al and Zn compounds. On the other hand, the sizable mass enhancement appears to be realized in PrIr$_2$Zn$_{20}$ under the fields near the quadrupole ordered phase boundary as indicated by the 100-fold increase of S/T and the large T^2 term of the electrical resistivity. Experimental identification of the field-induced exotic state remains an issue to be addressed.

Acknowledgments

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