Low temperature properties of ZrTr$_2$Zn$_{20}$ ($Tr =$ transition metal) with a pyrochlore lattice

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Abstract. Single crystals of ZrTr$_2$Zn$_{20}$ ($Tr =$ Mn, Co, Ru) with a cubic CeCr$_2$Al$_{20}$-type structure (space group Fd-3m) were grown by a Zn-flux method. Electrical resistivity $\rho(T)$ of ZrTr$_2$Zn$_{20}$ shows typical metallic behavior with the residual resistivity ratio (RRR) of 1.1 (Mn), 8.4 (Co) and 10 (Ru). Magnetic susceptibility $\chi(T)$ of ZrRu$_2$Zn$_{20}$ shows large diamagnetism. $\chi(T)$ of ZrTr$_2$Zn$_{20}$ ($Tr =$ Mn, Co) clearly shows Curie-Weiss behavior, indicating that Mn/Co spins are really active as local magnetic moments or that a large spin fluctuation exists. $\chi(T)$ of ZrMn$_2$Zn$_{20}$ increases ferromagnetically at around 20 K. Because the anti-ferromagnetic correlation with active localized spins exists in ZrCo$_2$Zn$_{20}$, geometrical frustration of the pyrochlore lattice of Co is expected. However, specific heat $C(T)$ of ZrCo$_2$Zn$_{20}$ shows no upturn at low temperatures and Sommerfeld coefficient $\gamma$ is evaluated to be 24.8 mJ/(mol K$^2$). We consider that the localized Co spins are insufficient to cause anomaly originated from the geometrical frustration, or the Co spins exist in a disordered arrangement of excess Co.

1. Introduction

Heavy-fermion behavior is one of the central issues in the strongly correlated systems. In this system, 4/5f electron plays an important role to form heavy-fermion state ascribed to competition between Kondo effect and RKKY interaction. However, heavy-fermion behavior without 4/5f-electron has been discovered in the pyrochlore compound LiV$_2$O$_4$ [1], where the heavy-fermion behavior is considered to be ascribed to the geometrical frustration on the pyrochlore lattice.

YMn$_2$Zn$_{20-x}$In$_x$ is an itinerant-electron antiferromagnet with magnetic Mn atoms forming a pyrochlore lattice made of corner-sharing tetrahedra [2]. This compound is also known to show heavy-fermion behavior. Specific heat $C(T)$ at low temperatures increases below 2 K and reaches 280 mJ/(mol K$^2$), suggesting a significant large mass enhancement. However, YMn$_2$Zn$_{20-x}$In$_x$ has a possibility that disorder from excess Mn mask intrinsic behavior [2]. Thus, at this stage, it is highly desirable to find a pure single crystal of MTr$_2$Zn$_{20}$ comprising Tr ($Tr =$ transition metal) pyrochlore lattice without excess magnetic elements.

We focus on Zr-based compounds ZrTr$_2$Zn$_{20}$, which can be synthesized without In substitution, and we report the physical properties of the single crystals of ZrTr$_2$Zn$_{20}$ ($Tr =$ Mn, Co, Ru).
2. Experimental details
Single crystals of Zr-Tr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru) were grown by a Zn-flux method. Zr chips, Mn, Co, and Ru powder, Zn grains were mixed in a molar ratio of 1:2:80. Each mixture sealed in silica tubes were heated on 1000$^\circ$C for 24h, and then cooled down to 500$^\circ$C at a rate of 5$^\circ$C/h in an electrical furnace. Zn-flux was eliminated by a centrifugation and the remaining one removed by acetic acid (0.1 %). The typical size of the single crystals is about 1 ~ 5 mm as shown in inset of Figure 1. The crystal structure was examined by the powder X-ray diffraction (XRD) technique with Cu-K$_\alpha$ radiation and a graphite monochromator (RAD-2X, Rigaku). The intensity data were collected over a 2$\theta$ range of 10-90$^\circ$ with a step width of 0.01$^\circ$ and a counting rate of 4$^\circ$/minutes. Magnetic susceptibility $\chi(T)$ measurements were performed by a magnetic properties measurements system (MPMS, Quantum Design). Electrical resistivity $\rho(T)$ was measured by an ac-four-probe method in a $^3$He cryostat (Heliox VL, Oxford) down to 0.3 K. Specific heat $C(T)$ measurements were performed down to 0.3 K in the $^3$He cryostat using a standard adiabatic heat-pulse method.

3. Experimental results
3.1. Chemical composition and lattice constants
Figure 1 shows the XRD patterns of Zr-Tr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru). Remaining Zn-flux is detected in the XRD patterns of ZrRu$_2$Zn$_{20}$. All peaks except for the Zn peaks can be indexed with a cubic unit cell with a space group Fd-3m. The lattice constants obtained from all indexes are 1.4033(2) (Mn), 1.3913(1) (Co) and 1.4038(1) nm (Ru). These values are in a good agreement with those of the previous report [3].

![Figure 1. XRD patterns of Zr-Tr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru) single crystal. Inset shows image of a single crystal of ZrRu$_2$Zn$_{20}$.](image-url)
3.2. Magnetic properties

Figure 2 (a) represents $T$-dependence of $\chi_0$ subtracted magnetic susceptibility $\chi(T) - \chi_0$ of ZrMn$_2$Zn$_{20}$, where $\chi_0$ is a $T$-independent term of $1.82 \times 10^{-3}$ emu/mol, and Figure 2 (b) shows $\chi(T)$ of ZrTr$_2$Zn$_{20}$ ($Tr = Co, Ru$) in a magnetic field of 0.1 T down to 2 K. $\chi(T)$ of ZrTr$_2$Zn$_{20}$ ($Tr = Mn, Co$) clearly shows Curie-Weiss behavior at high temperatures. This result indicates that Mn/Co spins are really active as local magnetic moments or that a large spin fluctuation exists. $\chi(T)$ of ZrMn$_2$Zn$_{20}$ ferromagnetically increase at $T_C \sim 20$ K. From $\chi' (T)$ in a temperature range of 100-300 K, Curie-Weiss fits give an effective moment of $\mu_{eff} = 0.68 \mu_B$/Mn and Curie temperature $\theta_C = 33$ K for ZrMn$_2$Zn$_{20}$, $\mu_{eff} = 1.1 \mu_B$/Co and Weiss temperature $\theta_w = -96$ K for ZrCo$_2$Zn$_{20}$. The estimated $\mu_{eff}$ values are relatively smaller than that expected when each Mn/Co atom carries an $S = 1/2$ localized spin ($\mu_{eff} = 1.73 \mu_B$/Tr), and are comparable to that of paramagnetic compounds $R$Fe$_2$Zn$_{20}$ ($R = Y, Lu$) [4]. Because localized spin exists ferromagnetically, geometrical frustration of the pyrochlore lattice of Mn cannot be expected in ZrMn$_2$Zn$_{20}$. On the other hand, ZrCo$_2$Zn$_{20}$ has a possibility of heavy-fermion behavior originated from geometrical frustration, because the anti-ferromagnetic correlation with active localized spin exists. $\chi(T)$ of ZrRu$_2$Zn$_{20}$ shows diamagnetism from room temperature. The diamagnetism is relatively large. Such a large diamagnetism is also seen in $AV_2Al_20$ ($A = Y, La$) [5].

![Figure 2](image)

Figure 2. (a) Magnetic susceptibility $\chi(T)$ and inverse susceptibility $\chi^{-1}(T)$ subtracted a temperature-independent term $\chi_0$ of ZrMn$_2$Zn$_{20}$ in a magnetic field of 0.1 T. (b) $\chi(T)$ and $\chi^{-1}(T)$ of ZrCo$_2$Zn$_{20}$ and $\chi(T)$ of ZrRu$_2$Zn$_{20}$ in a magnetic field of 0.1 T. The dotted line on each $\chi^{-1}$ data represents a Curie-Weiss fit.

3.3. Specific heat

Figure 3 shows $T$-dependence of specific heat $C(T)$ divided by $T$ of ZrTr$_2$Zn$_{20}$ ($Tr = Mn, Co, Ru$) down to 0.3 K. $C(T)/T$ can be fitted as $C/T = \gamma + \beta T^2$; $\gamma$ is Sommerfeld coefficient and $\beta$ is lattice specific coefficient. The fittings give $\gamma = 29.6$ and $\beta = 2.90$ (Mn), 24.8 and 1.32 (Co), 13.6 mJ/(mol K$^2$) and 1.53 mJ/(mol K$^4$) (Ru). From the simple Debye model of the phonon contribution with the relationship $\Theta_D = (12\pi^2 nR/5\beta)^{1/3}$, gas constant $R = 8.314$ J/(mol K) and $n = 23$ for ZrTr$_2$Zn$_{20}$, Debye temperatures $\Theta_D$ are evaluated to be 249 (Mn), 324 (Co) and 308 K (Ru), respectively. In the heavy fermion compounds originated from geometrical frustration, $C(T)/T$ shows upturn at low temperatures and reaches 207 mJ/(mol K$^2$) in YMn$_2$Zn$_{20}$, $\gamma$ is comparable to that of the normal and paramagnetic compounds in 1-2-20 system [5], heavy-fermion behavior is not observed in ZrCo$_2$Zn$_{20}$. The reason why upturn or large $\gamma$ is not
seen in ZrCo$_2$Zn$_{20}$ is not clear. One of the reasons is that the localized Co spins are insufficient to cause anomaly originated from the geometrical frustration. In the case of YMn$_2$(Zn$_{1-x}$In$_x$)$_{20}$, $\mu_{\text{eff}}$ is estimated to be 2.4 $\mu_B$/Mn, which is comparable to that expected when each Mn atom carries an $S = 1$ localized spin [2]. The estimated localized spin of ZrCo$_2$Zn$_{20}$ (1.1 $\mu_B$/Co) seems to be small to lead to anomaly originated from geometrical frustration. Another reason is that the localized Co spin is not located in the pyrochlore lattice, but exists in a disordered arrangement of excess Co in the compound. It is necessary to determine whether excess Co exists or not by means of detailed crystal structure analysis.

**Figure 3.** Temperature dependence of specific heat divided by temperature $C(T)/T$ of ZrTr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru). The dotted lines represent the fitting result (see text).

### 3.4. Electrical resistivity

Figure 4 shows $T$-dependence of electrical resistivity $\rho(T)$ of ZrTr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru) down to 0.29 K. $\rho(T)$ of ZrTr$_2$Zn$_{20}$ shows normal metallic behavior, although $\rho_0$ of ZrMn$_2$Zn$_{20}$ is relatively large. Residual resistivity ratios (RRR) are estimated to be 1.1 (Mn), 8.4 (Co) and 10 (Ru) respectively. The RRR of ZrMn$_2$Zn$_{20}$ is smaller than those of ZrTr$_2$Zn$_{20}$ (Tr = Co, Ru). In $\rho(T)$ of ZrMn$_2$Zn$_{20}$, anomaly ascribed to ferromagnetic transition is not observed. The $\rho(T)$ of ZrMn$_2$Zn$_{20}$ is quite similar to that of YMn$_2$Zn$_{20-x}$In$_x$ ($x = 3.44$), which is disordered by substitution of In and excess Mn. Large $\rho_0$ of ZrMn$_2$Zn$_{20}$ seems to be originated from disorder due to excess Mn [4].

**Figure 4.** Temperature dependence of electrical resistivity $\rho(T)$ of ZrTr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru).
4. Conclusion

We succeeded in synthesizing single crystals of ZrTr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru). ZrMn$_2$Zn$_{20}$ shows ferromagnetic transition at $T_C \sim 20$ K. $\rho(T)$ of ZrMn$_2$Zn$_{20}$ is metallic, but RRR is small and $\rho_0$ is large despite single crystal. This result indicates that excess Mn exists. Upturn in $C(T)/T$ at low temperatures is not observed above 0.3 K in ZrTr$_2$Zn$_{20}$ (Tr = Mn, Co, Ru). Magnetic susceptibility $\chi(T)$ of ZrRu$_2$Zn$_{20}$ shows large diamagnetism, which is very similar to that of AV$_2$Al$_{20}$ (A = Y, La). $\chi(T)$ of ZrTr$_2$Zn$_{20}$ (Tr = Mn, Co) clearly shows Curie-Weiss behavior. The results indicate that Mn/Co spins are really active as local magnetic moments or that a large spin fluctuation exists. $\chi(T)$ of ZrMn$_2$Zn$_{20}$ ferromagnetically increase at around 20 K. On the other hand, geometrical frustration of the pyrochlore lattice with Co can be expected in ZrCo$_2$Zn$_{20}$, because the anti-ferromagnetic correlation with active localized spins exists. However, $C(T)/T$ of ZrCo$_2$Zn$_{20}$ shows normal metallic behavior. We consider that the localized Co spins are insufficient to cause anomaly originated from the geometrical frustration, or the Co spins exist in a disordered arrangement of excess Co.

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