Low temperature properties of $ZrTr_2Zn_{20}$ (*Tr* = transition metal) with a pyrochlore lattice

S Hasegawa[1], K Morihiro[2], N Kase[1], T Nakano[1] and N Takeda[2]
[1]Graduate School of Science and Technology, Niigata University, Niigata 950-2102, Japan
[2]Department of Materials Science and Technology, Niigata University, Niigata 950-2102, Japan

E-mail: f15b032b@mail.cc.niigata-u.ac.jp

Abstract. Single crystals of $ZrTr_2Zn_{20}$ (*Tr* = Mn, Co, Ru) with a cubic $CeCr_2Al_{20}$-type structure (space group *Fd*-3*m*) were grown by a Zn-flux method. Electrical resistivity $\rho(T)$ of $ZrTr_2Zn_{20}$ 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 $ZrRu_2Zn_{20}$ shows large diamagnetism. $\chi(T)$ of $ZrTr_2Zn_{20}$ (*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 $ZrMn_2Zn_{20}$ increases ferromagnetically at around 20 K. Because the anti-ferromagnetic correlation with active localized spins exists in $ZrCo_2Zn_{20}$, geometrical frustration of the pyrochlore lattice of Co is expected. However, specific heat $C(T)$ of $ZrCo_2Zn_{20}$ shows no upturn at low temperatures and Sommerfeld coefficient γ 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, 4/5*f* electron plays an important role to form heavy-fermion state ascribed to competition between Kondo effect and RKKY interaction. However, heavy-fermion behavior without 4/5*f*-electron has been discovered in the pyrochlore compound LiV_2O_4 [1], where the heavy-fermion behavior is considered to be ascribed to the geometrical frustration on the pyrochlore lattice.

$YMn_2Zn_{20-x}In_x$ 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, $YMn_2Zn_{20-x}In_x$ 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_2Zn_{20} comprising *Tr* (*Tr* = transition metal) pyrochlore lattice without excess magnetic elements.

We focus on Zr-based compounds $ZrTr_2Zn_{20}$, which can be synthesized without In substitution, and we report the physical properties of the single crystals of $ZrTr_2Zn_{20}$ (*Tr* = Mn, Co, Ru).

2. Experimental details

Single crystals of $ZrTr_2Zn_{20}$ (*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°C for 24h, and then cooled down to 500°C at a rate of 5°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_α radiation and a graphite monochromator (RAD-2X, Rigaku). The intensity data were collected over a 2θ range of 10-90° with a step width of 0.01° and a counting rate of 4°/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 $ZrTr_2Zn_{20}$ (*Tr* = Mn, Co, Ru). Remaining Zn-flux is detected in the XRD patterns of $ZrRu_2Zn_{20}$. All peaks except for the Zn peaks can be indexed with a cubic unit cell with a space group *Fd*-3*m*. 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].

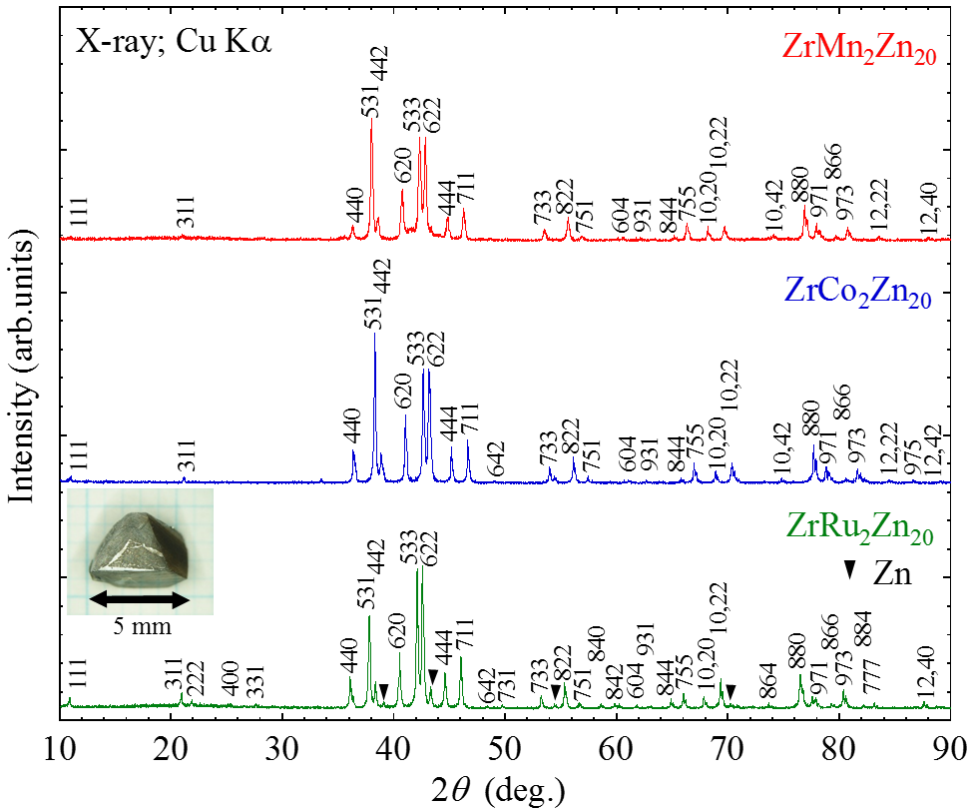

Figure 1. XRD patterns of $ZrTr_2Zn_{20}$ (*Tr* = Mn, Co, Ru) single crystal. Inset shows image of a single crystal of $ZrRu_2Zn_{20}$.

3.2. Magnetic properties

Figure 2 (a) represents T-dependence of χ_0 subtracted magnetic susceptibility $\chi(T)$ - χ_0 of $ZrMn_2Zn_{20}$, where χ_0 is a T-independent term of 1.82×10^{-3} emu/mol, and Figure 2 (b) shows $\chi(T)$ of $ZrTr_2Zn_{20}$ (Tr = Co, Ru) in a magnetic field of 0.1 T down to 2 K. $\chi(T)$ of $ZrTr_2Zn_{20}$ (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 $ZrMn_2Zn_{20}$ ferromagnetically increase at $T_C \sim 20$ K. From $\chi^{-1}(T)$ in a temperature range of 100-300 K, Currie-Weiss fits give an effective moment of $\mu_{eff} = 0.68\ \mu_B$/Mn and Currie temperature $\theta_C = 33$ K for $ZrMn_2Zn_{20}$, $\mu_{eff} = 1.1\ \mu_B$/Co and Weiss temperature $\theta_w = -96$ K for $ZrCo_2Zn_{20}$. The estimated μ_{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 RFe_2Zn_{20} (R = Y, Lu) [4]. Because localized spin exists ferromagnetically, geometrical frustration of the pyrochlore lattice of Mn cannot be expected in $ZrMn_2Zn_{20}$. On the other hand, $ZrCo_2Zn_{20}$ has a possibility of heavy-fermion behavior originated from geometrical frustration, because the anti-ferromagnetic correlation with active localized spin exists. $\chi(T)$ of $ZrRu_2Zn_{20}$ 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].

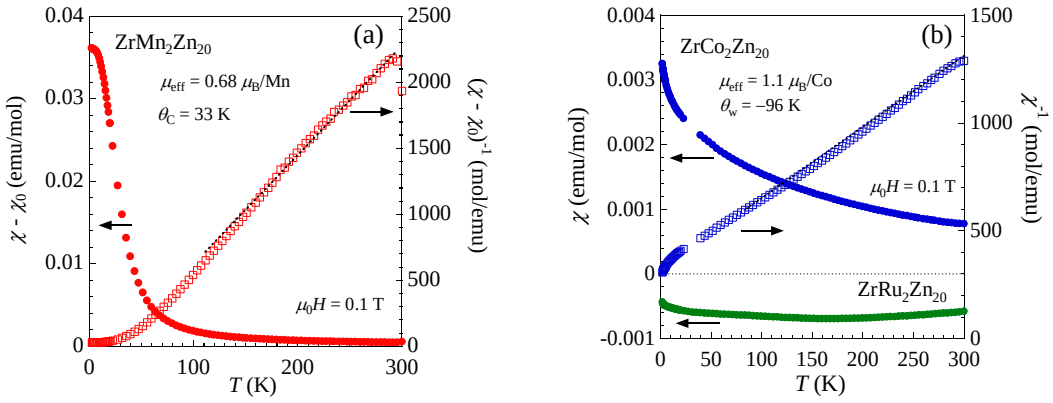

Figure 2. (a) Magnetic susceptibility $\chi(T)$ and inverse susceptibility $\chi^{-1}(T)$ subtracted a temperature-independent term χ_0 of $ZrMn_2Zn_{20}$ in a magnetic field of 0.1 T. (b) $\chi(T)$ and $\chi^{-1}(T)$ of $ZrCo_2Zn_{20}$, and $\chi(T)$ of $ZrRu_2Zn_{20}$ in a magnetic field of 0.1 T. The dotted line on each χ^{-1} data represents a Currie-Weiss fit.

3.3. Specific heat

Figure 3 shows T-dependence of specific heat $C(T)$ divided by T of $ZrTr_2Zn_{20}$ (Tr = Mn, Co, Ru) down to 0.3 K. $C(T)/T$ can be fitted as $C/T = \gamma + \beta T^2$; γ is Sommerfeld coefficient and β 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 $\Theta_D = (12\pi^4 nR/5\beta)^{1/3}$, gas constant $R = 8.314$ J/(mol K) and $n = 23$ for $ZrTr_2Zn_{20}$, Debye temperatures Θ_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 $YMn_2Zn_{20-x}In_x$ [2]. Because $C(T)/T$ of $ZrCo_2Zn_{20}$ shows no upturn at low temperature and γ is comparable to that of the normal and paramagnetic compounds in 1-2-20 system [5], heavy-fermion behavior is not observed in $ZrCo_2Zn_{20}$. The reason why upturn or large γ is not

seen in $ZrCo_2Zn_{20}$ 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 $YMn_2(Zn_{1-x}In_x)_{20}$, μ_{eff} is estimated to be 2.4 μ_B/Mn, which is comparable to that expected when each Mn atom carries an $S = 1$ localized spin [2]. The estimated localized spin of $ZrCo_2Zn_{20}$ (1.1 μ_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.

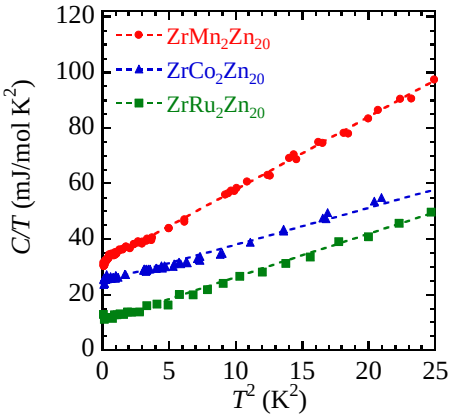

Figure 3. Temperature dependence of specific heat divided by temperature $C(T)/T$ of $ZrTr_2Zn_{20}$ (Tr = Mn, Co, Ru). The dotted lines represent the fitting result (see text).

3.4. Electrical resistivity

Figure 4 shows T-dependence of electrical resistivity $\rho(T)$ of $ZrTr_2Zn_{20}$ (Tr = Mn, Co, Ru) down to 0.29 K. $\rho(T)$ of $ZrTr_2Zn_{20}$ shows normal metallic behavior, although ρ_0 of $ZrMn_2Zn_{20}$ is relatively large. Residual resistivity ratios (RRR) are estimated to be 1.1 (Mn), 8.4 (Co) and 10 (Ru) respectively. The RRR of $ZrMn_2Zn_{20}$ is smaller than those of $ZrTr_2Zn_{20}$ (Tr = Co, Ru). In $\rho(T)$ of $ZrMn_2Zn_{20}$, anomaly ascribed to ferromagnetic transition is not observed. The $\rho(T)$ of $ZrMn_2Zn_{20}$ is quite similar to that of $YMn_2Zn_{20-x}In_x$ (x = 3.44), which is disordered by substitution of In and excess Mn. Large ρ_0 of $ZrMn_2Zn_{20}$ seems to be originated from disorder due to excess Mn [4].

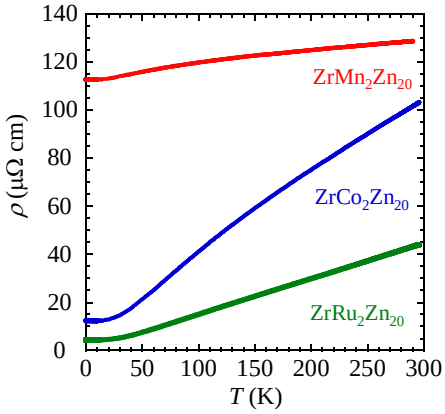

Figure 4. Temperature dependence of electrical resistivity $\rho(T)$ of $ZrTr_2Zn_{20}$ (Tr = Mn, Co, Ru).

4. Conclusion

We succeeded in synthesizing single crystals of $ZrTr_2Zn_{20}$ (*Tr* = Mn, Co, Ru). $ZrMn_2Zn_{20}$ shows ferromagnetic transition at $T_C \sim 20$ K. $\rho(T)$ of $ZrMn_2Zn_{20}$ is metallic, but RRR is small and ρ_0 is large despite single crystal. This result indicatives that excess Mn exists. Upturn in $C(T)/T$ at low temperatures is not observed above 0.3 K in $ZrTr_2Zn_{20}$ (*Tr* = Mn, Co, Ru). Magnetic susceptibility $\chi(T)$ of $ZrRu_2Zn_{20}$ shows large diamagnetism, which is very similar to that of AV_2Al_{20} (A = Y, La). $\chi(T)$ of $ZrTr_2Zn_{20}$ (*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 $ZrMn_2Zn_{20}$ ferromagnetically increase at around 20 K. On the other hand, geometrical frustration of the pyrochlore lattice with Co can be expected in $ZrCo_2Zn_{20}$, because the anti-ferromagnetic correlation with active localized spins exists. However, $C(T)/T$ of $ZrCo_2Zn_{20}$ 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.

Acknowledgments

This work was partially supported by the Grant-in-Aid for Young Scientist (B) (No. 26800183) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, the Sasakawa Scientific Research Grant (26-207) from the Japan Science Society, and the Uchida Energy Science Promotion Foundation (26-1-22).

References

[1] Kondo S, Johnston D C, Swenson C A, Borsa F, Mahajan A V, Miller L L, Gu T, Goldman A I, Maple M B, Gajewski D A, Freeman E J, Dilley N R, Dickey R P, Merrin J, Kojima K, Luke G M, Umemura Y J, Chmaissem O and Jorgensen J D 1997 *Phys. Rev. Lett.* **78** 3729
[2] Okamoto Y, Simizu T, Yamamura J, Kiuchi Y and Hiroi Z 2010 *J. Phys. Soc. Jpn.* **79** 093712
[3] Gross N, Nasch T and Jeitschko W 2001 *J. Solid State Chem.* **161** 288
[4] Jia S, Ni N, Bud'ko S L and Canfield P C 2009 *Phys. Rev.* B **80** 104403
[5] Onosaka A, Okamoto Y, Yamaura J, Hirose T and Hiroi Z 2012 *J. Phys. Soc. Jpn.* **81** 123702