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# Zn-site Substitution Effect in $YbCo_2Zn_{20}$

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**Abstract.**

We have investigated the substitution effect of $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems by using the experiments of X-ray powder diffraction (XRPD), specific heat, magnetic susceptibility, magnetization, and electrical resistivity in order to find out a material that approaches a quantum critical point by chemical pressure. The XRPD and electrical resistivity measurements clarify that the Cu-substitution makes the lattice constants shrink and keeps the magnetic electrical resistivity high, while the Ga- and the Cd-substitution show opposite relation of the Cu-substitution. However, we could not detect clear substitution effect in the specific heat, magnetic susceptibility, and magnetization measurements of Cu-substitution system within our experiments. It is necessary that to study the Cu-substitution samples that have higher $x$ value at lower temperature.

## Introduction

While the characteristic of heavy fermion ytterbium (Yb) compounds are similar to that of cerium (Ce) compounds due to the electron-hole analogy, there is a clear difference between two groups regarding the quantum critical behaviour, as reported in the study of $\beta$-$YbAlB_4$ and $YbRh_2Si_2$[1, 2]. This difference invokes fundamental interest to study the heavy fermion Yb compounds which are located near the quantum critical point (QCP).

A recently discovered $YbCo_2Zn_{20}$ is one of the most suitable material to investigate the QCP of Yb compounds. The Cubic $CeCr_2Al_{20}$-type ($Fd\bar{3}m$ space group) $YbCo_2Zn_{20}$, which has no magnetic order at ambient pressure, has extremely large value of electronic specific heat coefficient ($\gamma \simeq 8$ J/molK$^2$), and shows the field-induced order when the magnetic field only applies parallel to [111] direction[3, 4]. Especially, the existence of such a large $\gamma$ value implies that the compound is located near the QCP, which means that we can easily access to the QCP of that. In fact, it was reported that an antiferromagnetic order was induced by the pressure of 1.5 GPa which is the lowest value in Yb compounds, except for $\beta$-$YbAlB_4$[5, 1]. Therefore, there is the possibility that chemical pressure also tunes the ground state to the magnetic one

**Table 1.** The actual value of $x$ in three substitution systems estimated by ICP-AES.

| nominal (%) | ICP-AES results (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | | | Ga | | | Cd | | |
| | $C_{\rm mag}$ | $M, \chi_{\rm dc}$ | $\rho_{\rm mag}$ | $C_{\rm mag}$ | $M, \chi_{\rm dc}$ | $\rho_{\rm mag}$ | $C_{\rm mag}$ | $M, \chi_{\rm dc}$ | $\rho_{\rm mag}$ |
| 2.5 | 1.9 | 1.9 | 1.9 | 3.3 | 3.2 | 3.2 | 1.4 | 1.3 | 1.4 |
| 5.0 | 2.5 | | 2.5 | 6.0 | 6.0 | 6.0 | 2.5 | 2.4 | 2.2 |

and/or the QCP. While a large number of study of $YbCo_2Zn_{20}$ has been performed up to now, there is no information about the chemical pressure by substitution. Very recently, we have succeeded in growing single crystals where Co- and Zn-site of $YbCo_2Zn_{20}$ are substituted by several materials.

In this paper, we have focused on the substitution effect of Zn-site in $YbCo_2Zn_{20}$ in order to explore the material that approach QCP by chemical pressure. We have investigated $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Gd) systems by using the measurements of the X-ray powder diffraction (XRPD), specific heat, magnetic susceptibility, magnetization, and electrical resistivity.

## Experimental

Single crystals of $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Gd) were grown by an Zn self-flux method. Materials where stoichiometric ratio of Yb : Co : Zn : $T$ ($T$ = Cu, Ga, and Cd) are $1 : 2 : 30(1-x) : x$ ($x$ = 0.025 and 0.05) were placed in an alumina crucible, sealed in a quartz ampule, heated up to 950 °C, and then cooled down to 750 °C at a rate of 1 °C/h. The Zn flux was removed by centrifugation. Almost obtained single crystals have a shining crystal-growth-plane perpendicular to the [111] direction.

In order to check the actual value of $x$, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed. We picked up tiny pieces of the single crystals from the surrounding samples that was used for the experiments explained in the next paragraph. The actual values of $x$ in three substitution systems which were estimated by ICP-AES are summarized in Table 1. The results of ICP-AES indicate that $x$ are smaller than the nominal one, except for the Ga-substitution system.

All obtained samples were measured by using XRPD, specific heat, magnetic susceptibility, magnetization, and electrical resistivity. The XRPD measurements were performed at room temperature using single crystals powdered. The specific heat, magnetic susceptibility, magnetization, and electrical resistivity measurements were performed in the temperature range between 2.0 and 300 K by means of PPMS and SQUID magnetometer MPMS commercial equipment (Quantum Design).

## Results and Discussion

Figure 1 (Left) indicates $x$ dependence of the lattice constants for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. In Cu-substitution system, the lattice constant decreases with $x$, while it increases with $x$ in Ga- and Cd-substitution systems. The results indicate the existence of positive chemical pressure in Cu-substitution system.

Figure 1 (Right) represents temperature dependence of the magnetic component of specific heat ($C_{\rm mag}$) in the form of $C_{\rm mag}/T$ for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The $C_{\rm mag}$ is obtained by subtracting the specific heat of nonmagnetic $LuCo_2Zn_{20}$ from that

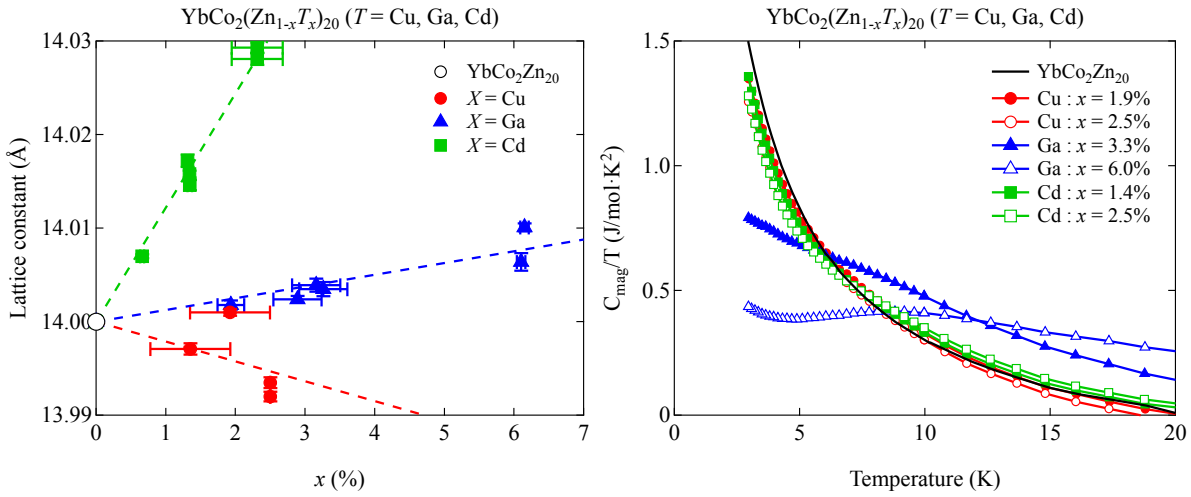


**Figure 1.** (Left) $x$ dependence of the lattice constants for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The open circle represents the lattice constant of the non-doped $YbCo_2Zn_{20}$. The filled circles, triangles, and squares indicate that of Cu-, Ga-, and Cd-substitution systems, respectively. (Right) Temperature dependence of the magnetic specific heat ($C_{\rm mag}$) in the form of $C_{\rm mag}/T$ for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The solid line represents the $C_{\rm mag}$ of the non-doped $YbCo_2Zn_{20}$. The solid and open circles, triangles, and squares indicate that of $x = 1.9\%$ (Cu), 2.5% (Cu), 3.3% (Ga), 6.0% (Ga), 1.4% (Cd), 2.5% (Cd), respectively.

data. In this temperature region, the $C_{\rm mag}$ does not change by Cu- and Cd-substitution. The Ga-substitution, which has relatively high $x$ value, suppresses the enhancement of $C_{\rm mag}$ at low temperature.

Figure 2 (Left) shows temperature dependence of the magnetic susceptibility ($\chi_{\rm dc}$) and the inverse magnetic susceptibility ($1/\chi_{\rm dc}$) for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The applied magnetic field is 1.0 T parallel to [111]. All the data can be fitted well by Curie-Weiss law above 100 K, yielding the effective magnetic moment ($\mu_{\rm eff}$) and paramagnetic Curie-Weiss temperature ($\theta_{\rm p}$), which are summarized in Table 2. There is no remarkable change in $\mu_{\rm eff}$ and $\theta_{\rm p}$ for all the substitution systems. The effect of these substitution for $\chi_{\rm dc}$ is weak.

Figure 2 (Right) indicates isothermal magnetization curve for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems at 2.0 K. The direction of applied magnetic field is parallel to [111]. The magnetization almost does not change by Cu- and Gd-substitution. The Ga-substitution in $x = 3.2$ and 6.0% suppress the magnetization. The magnetization shape of Cd-substitution in $x$ =2.4 seems to slightly different to that of other substitutions. This difference may come from misalignment of the single crystal sample.

Figure 3 shows temperature dependence of the magnetic electrical resistivity ($\rho_{\rm mag}$) for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The electrical current was applied parallel to [111]. The $\rho_{\rm mag}$ increases with decrease of temperature and then it makes the broad peak at $T_{\rho,\rm max}$ in the non-doped $YbCo_2Zn_{20}$. In three substitution systems however, the $T_{\rho,\rm max}$ disappears in this temperature region. The increase of $x$ does not change the $\rho_{\rm mag}$ in Cu-substitution system, while it suppress $\rho_{\rm mag}$ in Ga- and Cd-substitution systems.

The Cu-substitution system which shows the positive chemical pressure and keeps $\rho_{\rm mag}$ high is the only candidate to approach QCP in three substitution systems. However, to measure samples having higher $x$ value and/or to measure at lower temperature is required in order to

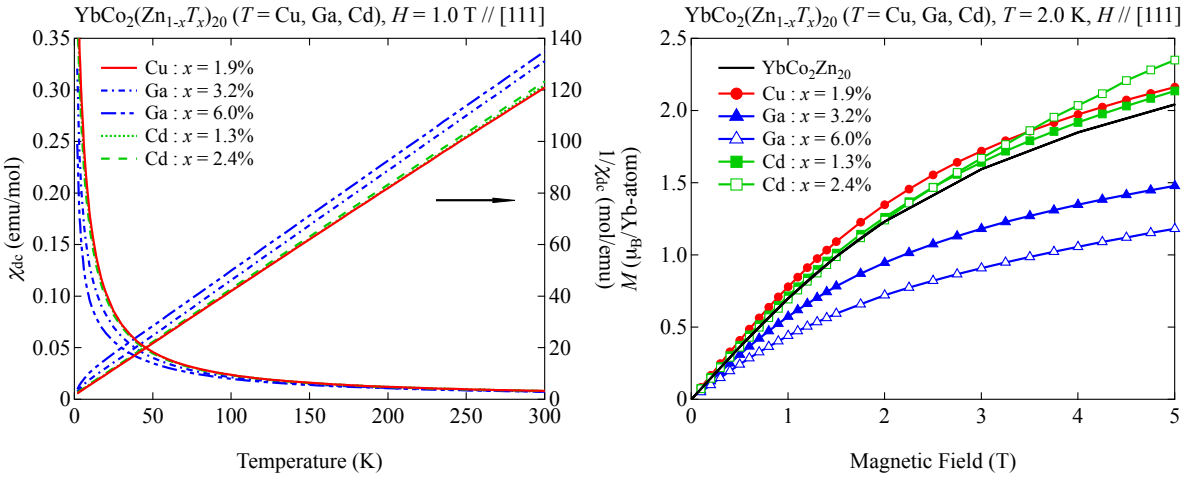


**Figure 2.** (Left) Temperature dependence of the magnetic susceptibility ($\chi_{\rm dc}$) and the inverse magnetic susceptibility ($1/\chi_{\rm dc}$) for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The solid, one-dot chain, and two-dot chain lines indicate that of $x = 1.9\%$ (Cu), 3.2% (Ga), 6.0% (Ga), 1.3% (Cd), and 2.4% (Cd), respectively. (Right) Isothermal magnetization curve for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems at 2.0 K. The solid line represents that of the non-doped $YbCo_2Zn_{20}$. The filled circles indicates that of $x = 1.9\%$ (Cu), and the filled and open triangles and squares show that of $x = 3.2\%$ (Ga), 6.0% (Ga), 1.3% (Cd), and 2.4% (Cd), respectively.

**Table 2.** The effective moment ($\mu_{\rm eff}$) and paramagnetic Curie-Weiss temperature ($\theta_{\rm p}$) for three substitution systems. [1]These values refer to Takeuchi's results[6].

| | $YbCo_2Zn_{20}$ | Cu: 1.9% | Ga: 3.2% | Ga: 6.0% | Cd: 1.3% | Cd: 2.4% |
|---|---|---|---|---|---|---|
| $\mu_{\rm eff}$ ($\mu_{\rm B}$) | 4.27[1] | 4.48(1) | 4.35(1) | 4.31(1) | 4.49(1) | 4.45(1) |
| $\theta_{\rm p}$ (K) | -1.43[1] | -4.4(1) | -9.0(1) | -13(1) | -6.5(1) | -5.2(1) |

know actual effect of Cu-substitution. There is no magnetic order at $x = 0 \sim 2.5\%$ in Cu-substitution system. The existence of chemical-pressure-induced magnetic order is one of the most strong evidence that the system crosses QCP. Therefore, to find that by measurement of higher $x$ value samples is important. In addition, we could not detect clear substitution effect in $C_{\rm mag}$ and $\chi_{\rm dc}$ measurements of Cu- and Cd-substitution systems within our experiments. These measurements at $T = 0.2 \sim 3$ K may clarify more detailed substitution effect.

## Summary

We have investigated the substitution effect of $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems by the measurements of XRPD, specific heat, magnetic susceptibility, magnetization, and electrical resistivity. The Cu-substitution makes the lattice constants shrink and keeps the $\rho_{\rm mag}$ high, while Ga- and Cd-substitutions show opposite relation of Cu-substitution. We could not detect clear substitution effect in $C_{\rm mag}$, $\chi_{\rm dc}$, and magnetization measurement of Cu-substitution system within our experiments, which imply that experiments at $T = 0.2 \sim 3$ K are

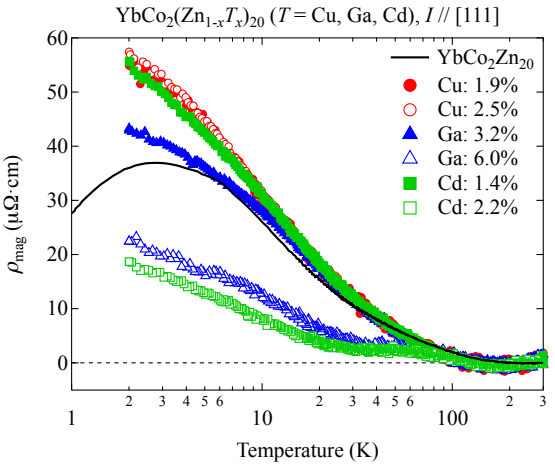


**Figure 3.** Temperature dependence of the magnetic electrical resistivity ($\rho_{\mathrm{mag}}$) for $YbCo_2(Zn_{1-x}T_x)_{20}$ ($T$ = Cu, Ga, and Cd) systems. The electrical current was applied parallel to [111]. The solid line shows that of the non-doped $YbCo_2Zn_{20}$. The filled and open circle, triangle, and square represent that of $x$ = 1.9% (Cu), 2.5% (Cu), 3.2% (Ga), 6.0% (Ga), 1.4% (Cd), and 2.2% (Cd), respectively.

necessary to understand more detailed substitution effect. To find the chemical-pressure-induced magnetic order in the samples of higher $x$ value is important to approach QCP.

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