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Magnetic Properties of Icosahedral (Au,Cu)–Al–Yb Quasicrystals

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We have synthesized Cu-substituted (Au,Cu)–Al–Yb quasicrystals in order to investigate the relationship between the quasilattice constant and the magnetic property. The quasilattice constant a_{R} is found to decrease as Au is replaced by Cu, and the maximum reduction of 2.18% in a_{R} was observed for $x = 0.60$ in $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$. Magnetic measurements of $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ (x = 0, 0.10, 0.20, 0.50) show that the intermediate-valence state of Yb persists in all the studied compositions. The effective magnetic moment is found to depend on $\bar{r}/a_{\mathrm{R}}$ rather than on the quasilattice constant a_{R}. This suggests that $\bar{r}/a_{\mathrm{R}}$ can be regarded as a measure of the chemical pressure induced on the Yb atoms.

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1. Introduction

After the discovery of the stable binary Tsai-type Cd–Yb quasicrystal [1, 2], icosahedral quasicrystals containing Yb have been found in many alloy systems such as Cd-Mg-Yb [3], Ag–In–Yb [4], Zn–Mg–Yb [5], Au–In–Yb [6]. Concerning the magnetism, it has turned out that these Yb containing quasicrystals have no magnetic moments since the valence of Yb ions in these quasicrystals is divalent at ambient pressure. However, in 2011, Ishimasa et al. reported that Yb is in the intermediate valence state at ambient pressure in the $\mathrm{Au}_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ quasicrystal [7, 8].

Meanwhile, Watanuki et al. attempted to increase the Yb valence by applying pressure to the icosahedral $\mathrm{Cd}_{23}\mathrm{Mg}_{61}\mathrm{Yb}_{16}$ [9]. They found that the Yb valence increases with pressure, suggesting that the decrease of the quasilattice constant may be a key to realize the intermediate valence state of Yb. Based on the high pressure work, we have substituted Cu into the Au site in order to further reduce the quasilattice constant since the atomic radius of Cu (1.278 Å) is much smaller than that of Au (1.442 Å) [10]. In this paper, we will discuss the factor which is responsible for the Yb valence by systematically evaluating the effective magnetic moment of the Cu-substituted quasicrystals.

2. Experimental details

Alloys with nominal compositions of $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ ($x = 0\ldots0.60$) were prepared using high-purity elements (Au (99.99 wt%), Cu (99.99 wt%), Al (99.999 wt%), and Yb (99.9 wt%)) in an arc furnace under an argon atmosphere. The phase purity of the samples was determined by powder X-ray diffraction using Cu K_α radiation (Rigaku Ultima III). The quasilattice constant a_{R} was evaluated from the position of the (2 1 1 1 1 1) peak. The magnetic susceptibility was measured between 2 and 300 K at 0.1 T using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS).

3. Sample characterization

Figure 1 shows powder X-ray diffraction patterns of the alloys with the nominal composition of $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ ($x = 0\div0.60$). As seen in Fig. 1, formation of the icosahedral phase is observed in all the samples, showing that the icosahedral phase forms in a wide composition range up to $x = 0.60$. Table I shows the obtained values of the (2 1 1 1 1 1) peak position (2θ), the quasilattice constant a_{R} and the contraction of the quasilattice compared to that of the unsubstituted $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ quasicrystal. It is seen that a_{R} decreases as x increases, and the largest decrease of 2.18% in a_{R} is obtained for the maximum substitution corresponding to $x = 0.60$. This result is well explained by the fact that the atomic radius of Cu (1.278 Å) is smaller than that of Au (1.442 Å).

4. Magnetic susceptibility

Magnetic properties were measured for the samples containing the icosahedral phase as the major phase. Figure 2 shows the inverse magnetic susceptibility $1/\chi(T)$ of $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ (x = 0, 0.10, 0.20, 0.50) as a function of temperature. Above 100 K, $\chi(T)$ well obeys the Curie–Weiss law,

$$\chi(T) = \frac{N_{\mathrm{A}}\mu_{\mathrm{eff}}^2\mu_{\mathrm{B}}^2}{3k_{\mathrm{B}}(T-\Theta_{\mathrm{p}})} + \chi_0,$$

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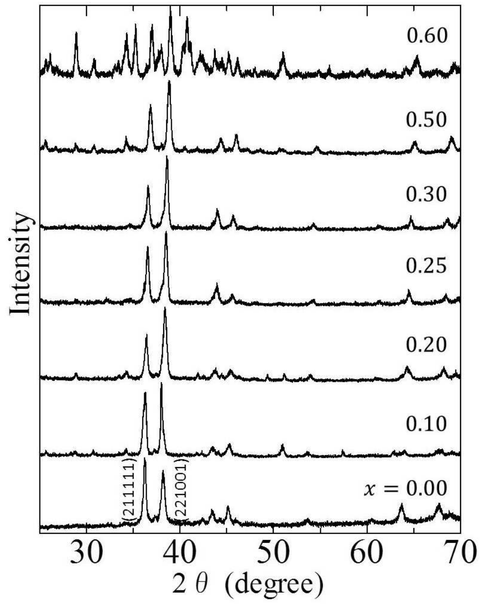

Fig. 1. Powder X-ray diffraction patterns of $(Au_{1-x}Cu_x)_{49}Al_{34}Yb_{17}$ alloys.

TABLE I

The (2 1 1 1 1 1) peak position (2Θ), the quasilattice constant a_R and the lattice contraction of $(Au_{1-x}Cu_x)_{49}Al_{34}Yb_{17}$ relative to the unsubstituted alloy.

x	2Θ (deg)	a_R (Å)	lattice contraction (%)
0.00	36.19	5.257	0.00
0.10	36.30	5.242	0.30
0.20	36.44	5.222	0.67
0.25	36.55	5.207	0.95
0.30	36.56	5.206	0.98
0.40	36.90	5.159	1.87
0.50	36.99	5.147	2.10
0.60	37.02	5.143	2.18

where k_B, N_A, μ_B, Θ_p, and χ_0 are the Boltzmann factor, the Avogadro number, the Bohr magneton, paramagnetic Curie temperature, and temperature independent susceptibility, respectively. Table II shows the parameters obtained from the fits for $(Au_{1-x}Cu_x)_{49}Al_{34}Yb_{17}$. As can be seen, all the effective moments are appreciably smaller than $\mu_{eff}(Yb^{3+})$ of 4.54 μ_B, where $\mu_{eff}(Yb^{3+})$ is the effective magnetic moment for the free Yb^{3+} ion. This implies that the intermediate valence state is maintained throughout the whole Cu substitutions into the Au site of Au–Al–Yb quasicrystals up to $x = 0.60$.

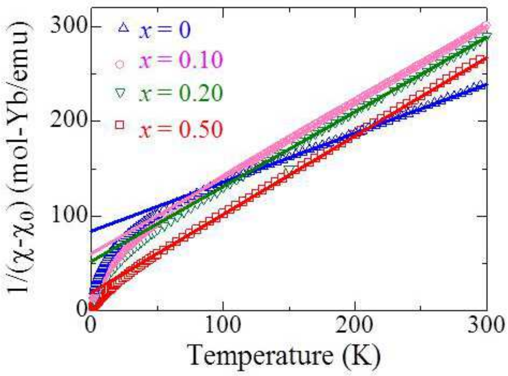

Fig. 2. The inverse magnetic susceptibility $1/\chi(T)$ of $(Au_{1-x}Cu_x)_{49}Al_{34}Yb_{17}$ as a function of temperature. Solid lines denote the Curie-Weiss fits.

TABLE II

Effective magnetic moment μ_{eff}, paramagnetic Curie temperature Θ_p and χ_0 obtained from the Curie-Weiss fits of $(Au_{1-x}Cu_x)_{49}Al_{34}Yb_{17}$.

x	μ_{eff} (μ_B)	Θ_p (K)	χ_0 (emu/mol Yb)
0.00	3.94	−164	-6.45×10^{-4}
0.10	3.21	−80.6	1.80×10^{-4}
0.20	3.19	−66.9	4.62×10^{-4}
0.50	3.10	−23.5	4.05×10^{-4}

5. Discussion

From the high pressure experiment on the $Cd_{23}Mg_{61}Yb_{16}$ quasicrystal a contraction of the quasilattice of about 2.7% was observed under 4 GPa, and the Yb valence was found to change from +2.0 to +2.1 [9]. This means that the Yb valence increases as the quasilattice constant decreases under applied pressure. The present study, however, shows that the effective magnetic moment which is a probe of the Yb valence decreases as the quasilattice constant a_R decreases as seen in Fig. 3. The result suggests that the reduction of a decrease in the quasilattice constant does not necessarily cause a stronger pressure on the Yb ions.

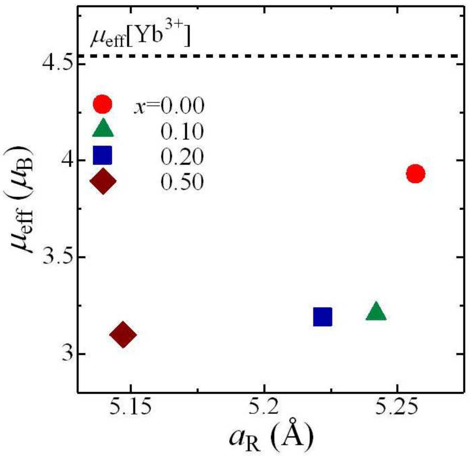

Fig. 3. Effective magnetic moment μ_{eff} of $(Au_{1-x}Cu_x)_{49}Al_{34}Yb_{17}$ as a function of the quasilattice constant a_R.

In order to understand the effect of chemical pressure on Yb ions, we use $\bar{r}/a_{\mathrm{R}}$ value of the Au–Cu–Al–Yb quasicrystals. Here, $\bar{r}$ and a_{R} stand for the average atomic radius of the constituent elements weighted over the nominal composition and the edge length of the rhombic triacontahedral (RTH) cluster, which is a building block of the Tsai-type icosahedral quasicrystals and thus gives a measure of the cluster size [11], respectively. For the estimation of $\bar{r}$, we used the atomic radius of divalent Yb (1.940 Å) [10]. In this way, the $\bar{r}/a_{\mathrm{R}}$ value is considered to be a better measure of the atomic packing factor of the quasicrystals than the quasilattice constant.

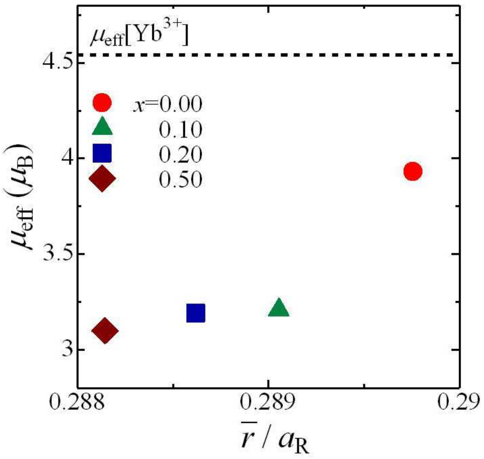

Fig. 4. Effective magnetic moment μ_{eff} of $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ as a function of the $\bar{r}/a_{\mathrm{R}}$ value.

Figure 4 shows the effective magnetic moments plotted against the $\bar{r}/a_{\mathrm{R}}$ value. It is seen that the effective magnetic moment increases as $\bar{r}/a_{\mathrm{R}}$ increases. This result shows that the increase of the $\bar{r}/a_{\mathrm{R}}$ value results in higher pressure upon the Yb atoms, suggesting that the $\bar{r}/a_{\mathrm{R}}$ value is a better indicator of the chemical pressure rather than the quasilattice constant a_{R} by itself.

6. Summary

An icosahedral quasicrystalline phase was found to form in the $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ alloy within a wide composition range up to $x = 0.60$. It was found that the quasilattice constant a_{R} decreases as Au is replaced by Cu. The maximum decrease of 2.18% in a_{R} was observed for $x = 0.60$. The magnetic properties of the compositions $(\mathrm{Au}_{1-x}\mathrm{Cu}_x)_{49}\mathrm{Al}_{34}\mathrm{Yb}_{17}$ ($x = 0, 0.10, 0.20, 0.50$) show that the intermediate valence state persists for all the studied compositions. Moreover, the effective magnetic moment μ_{eff} is found to depend on $\bar{r}/a_{\mathrm{R}}$ rather than on the quasilattice constant a_{R} by itself. This suggests that the $\bar{r}/a_{\mathrm{R}}$ value is a better indicator of chemical pressure.

Acknowledgments

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