Gold Substitution Effect on Structure and Superconductivity Properties in Filled Skutterudite La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$

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A series of single-phased La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ compounds were prepared by an arc-melting method. The crystal structure and basic superconductivity parameters have been systematically investigated by X-ray diffraction and by examining the temperature and field dependences of electrical resistivity, magnetization and heat capacity. The lattice parameter $a$ increases and the superconducting transition temperature $T_c$ decreases gradually with increasing Au content $x$. The low critical field $H_c1(T)$ and the upper critical field $H_{c2}(T)$ were estimated from the isothermal magnetization ($M$-$H$-$T$) and electrical transport ($p$-$H$-$T$) measurements, respectively. The evaluated $H_{c1}(0)$ and $H_{c2}(0)$ indicate a decrease tendency with increasing $x$, and enable us to deduce the coherence length $\xi(0)$, penetration depth $\lambda(0)$, Ginzburg-Landau parameter $\kappa(0)$ and thermodynamic critical field $H_c(0)$. The present results are compared with those of the related systems.

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1. Introduction

The filled skutterudite compounds with chemical formula RT$_4$X$_{12}$ (R = rare earth, T = Fe, Ru, Os etc. and X = P, As, Sb etc.) have attracted considerable attention due to both their thermoelectric applications.1–5) This compound is known to crystallize in a body centered cubic structure with the space group of Im3. Recently, a new family of skutterudites MPt$_4$Ge$_{12}$ (M = Sr, Ba, La, Ce, Eu, Nd, Pr, Th etc.) have been reported by several research groups.6–11) Interestingly, the compound with divalent cations of Sr or Ba is found to be superconducting below 5.1 and 5.35 K, respectively.6,7) The compound, PrPt$_4$Ge$_{12}$, has a $T_c$ of 7.9 K with trivalent Pr in a nonmagnetic ground state, almost as high as that of superconducting transition temperature of LaPt$_4$Ge$_{12}$ ($T_c = 8.3$ K).8) The isostructural ThPt$_4$Ge$_{12}$ was reported to be superconducting below 6.4 K.11) As well as in other superconductors,12–14) an elemental substitution serves as a useful tool to modify the structure and other physical properties of MPt$_4$Ge$_{12}$ system, and to study the underlying mechanism of superconductivity. Heterovalent substitution is considerable interesting, as they can change the total number of electrons and may be more effective in changing $T_c$. Most recently, Gumeniuk et al.15) theoretically and experimentally studied the electronic structure and physical properties in Ba(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ ($x = 0–0.25$). An increase tendency in $T_c$ from 5.0 K ($x = 0$) to 7.0 K ($x = 0.25$) was observed, which was consistent with the electronic structure calculations. For the MPt$_4$Ge$_{12}$ superconductors, the electronic structure calculation revealed that the Fermi level $E_F$ locates in a pronounced peak of the electronic density of state (DOS) for $M = $ La and Pr, whereas the $E_F$ level deviates from a peak for $M = $ Ba and Sr.6,7,15) The partial substitution of Au for Pt in LaPt$_4$Ge$_{12}$ may shift the $E_F$ level apart from the DOS peak, resulting in a decrease of DOS at $E_F$. If this is the case, the critical temperatures $T_c$ of La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ decrease by the substitution. This work aims to understand the gold substitution effect on filled skutterudites MPt$_4$Ge$_{12}$ superconductors in more detail via a study of the lattice parameter and superconducting transition temperature $T_c$, together with upper critical field $H_{c2}$, low critical field $H_{c1}$, coherence length $\xi(0)$, penetration depth $\lambda(0)$, Ginzburg-Landau parameter $\kappa(0)$ and thermodynamic critical field $H_c(0)$ in La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ ($x = 0–0.25$).

2. Experimental

The polycrystalline La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ ($x = 0–0.25$) were synthesised by an arc melting method using a tungsten electrode under an argon atmosphere. Stoichiometric amounts of high purity La, Pt, Au and Ge were melted more than six times for homogeneity on a water-cooled copper hearth. The total weight loss of the sample in this step was less than 0.5%. Then the samples were annealed in evacuated quartz tubes for one week at 1103 K ($x = 0$), 1053 K ($x = 0.05$ and 0.1), 903 K ($x = 0.15–0.25$), and then quenched in ice water. The samples were characterized by X-ray powder diffraction experimental (XRD). The magnetization measurements were carried out using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7). Temperature and field dependences of resistivity were measured by standard four-probe method using physical property measurement system (PPMS-9) from Quantum Design.

3. Results and Discussion

The XRD data were collected with all of the La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ samples. Only very small amount of Ge peak was observed within the experimental errors for $x < 0.2$. All the samples have a cubic crystal structure of LaFe$_4$P$_{12}$ type belonging to Im3$^-$ space group. Some unknown impurity peaks were found with further substitution for $x > 0.2$. The limiting solubility of Au substitution at Pt site in La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ system was in the range of 0.15–0.20. This behavior was similar to that of Ba(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$ system. The lattice parameter $a$ in La(Pt$_{1-x}$Au$_x$)$_4$Ge$_{12}$...
La(Pt\textsubscript{x}Au\textsubscript{1-x})\textsubscript{4}Ge\textsubscript{12} (M = La and Ba\textsuperscript{12}) x = 0–0.25) system.

Figure 2 shows the temperature dependences of normalized electrical resistivity $\rho(T)/\rho(10\text{K})$ and magnetization $M$ ($H = 5\text{ mT}$, under zero field cooling mode) for La(Pt\textsubscript{x}Au\textsubscript{1-x})\textsubscript{4}Ge\textsubscript{12} (x = 0–0.2) system from 2 K to 9 K. All the samples show a superconducting transition. The superconducting transition temperature $T_c$ was summarized in the inset of Fig. 2, where $T_c$ gradually decreases with increasing Au substitution content $x$. This is a contrary tendency to that of Ba(Pt\textsubscript{x}Au\textsubscript{1-x})\textsubscript{4}Ge\textsubscript{12} system. The temperature dependence of resistivity ($\rho$-$T$) at several externally applied fields (as shown in Fig. 3) and isothermal magnetization curve ($M$-$H$) at various temperatures (as shown in Fig. 4) were measured for La(Pt\textsubscript{x}Au\textsubscript{1-x})\textsubscript{4}Ge\textsubscript{12} (x = 0–0.2) system. The upper critical field $H_{c2}(T)$ was determined from the offset points of the transition temperature in the $\rho(T,H)$ curve. The temperature dependence of $H_{c2}(T)$ are shown in Fig. 5, which suggests that $H_{c2}$ varies almost linearly with $T$. Extrapolation to $T = 0\text{ K}$ with a linear fit of the experimental data for each sample results in $H_{c2}(0)_{\text{linear}}$ (as shown in the inset of Fig. 5). The values of $H_{c2}(0)_{\text{linear}}$ decrease from 1.88 to 1.03 T with increasing $x$ from 0 to 0.2. An alternating estimation of $H_{c2}(0)$ was carried out by the Werthamer–Helfand–Hohenberg (WHH) approximation of $H_{c2}(0)_{\text{WHH}} = 0.691 \times (dH_{c2}/dT)_{T_c} \times T_c$\textsuperscript{16}. The results of $H_{c2}(0)_{\text{WHH}}$ are also shown in the inset of Fig. 5. $H_{c2}(0)_{\text{WHH}}$ shows approximately the same $x$ dependence as that of $H_{c2}(0)_{\text{linear}}$ and decrease from 1.34 to 0.73 T. In the following calculations, we have used the $H_{c2}(0)_{\text{WHH}}$ value as that for $H_{c2}(0)$. Another important parameter characterizing superconductivity is the lower critical field $H_{c1}$. A value of $H_{c1}$ for certain $x$ and temperature was taken as the field at which $M(H)$ curve (in Fig. 4) deviates from the linear relation expected for the perfect diamagnetism. The $H_{c1}$ as a function of temperature is...
plotted in Fig. 6. The $H_c1(T)$ curve fitted with a relationship, $H_{c1} = H_{c1}(0) \times \left[1 - (T/T_c)^2\right]$, yields a $H_{c1}(0)$ value presented in the inset of Fig. 6. The values of $H_{c1}(0)$ decrease gradually from 23.9 to 13.3 mT with the increasing $x$ from 0 to 0.2.

From the upper critical field, we estimated the coherence length, $\xi(0)$, using the formula, $H_{c2} = \Phi_0/(2\pi \xi^2)$, where $\Phi$ is the flux quantum. The estimation results of $\xi(0)$ as a function of $x$ for La(Pt$_{1-x}$Au$_x$)$_3$Ge$_{12}$ ($x = 0$–0.2) system are shown in Fig. 7(a). The values of $\xi(0)$ increase gradually from 13.2 to 17.9 nm with increasing $x$, and are larger than those of Li$_2$(Pd$_{1-x}$Ni$_x$)$_3$B (8.5–12.3 nm) system$^{17}$ and typical high-$T_c$ superconductors ($\sim$ 2 nm). The relatively large coherence length means the present system is a classic superconductor without "weak links". From $H_{c1}(0)$ and $\xi(0)$, the penetration depth, $\lambda(0)$ (Fig. 7(b)), were calculated using the formula, $H_{c1} = \Phi_0/4\pi \lambda^2 \times \ln(\lambda/\xi)$. The values of $\lambda(0)$ increase from 124 nm to 166 nm, and comparable with that of Li$_2$Pd$_3$B (132 nm).$^{17}$ The Ginzburg-Landau parameter $\kappa(0)$ is in the range of 7.9–9.4, derived from the relation, $\kappa = \lambda/\xi$ (Fig. 7(c)). These values are a little lower than those of Li$_2$Pd$_3$B ($\kappa(0) = 15.5$)$^{17}$ Re$_2$B$_3$ ($\kappa(0) = 17$)$^{18}$ and MgB$_2$ ($\kappa(0) = 20$)$^{19}$ but they are much more lower than that of Mo$_7$Re$_{13}$X (X = B, C) ($\kappa(0) \sim 100$)$^{20}$ The thermodynamic critical field $H_{c1}(0)$ were calculated using the formula, $H_{c1}(0) = H_{c2}(0)/\sqrt{2}\xi(0)$, as shown in the Fig. 7(d). The values of $H_{c1}(0)$ decrease from 0.614 to 0.338 T with the increasing of $x$. 
4. Conclusions

In summary, we have been systematically studied the crystal structure and basic superconductivity parameters in La(Pt\textsubscript{1-x}Au\textsubscript{x})\textsubscript{4}Ge\textsubscript{12} system. The limiting solubility of Au substitution at Pt site was less than 0.20. The superconducting transition temperature $T_c$ decrease gradually with increasing Au content $x$, which is in contrast to that of Ba(Pt\textsubscript{1-x}Au\textsubscript{x})\textsubscript{4}Ge\textsubscript{12} system. The temperature dependence of low critical field $H_{c1}$ and upper critical field $H_{c2}$ were estimated and the calculated $H_{c1}(0)$ and $H_{c2}(0)$ decrease continuously with the increases of $x$. The coherence length $\xi(0)$, penetration depth $\lambda(0)$, Ginzburg-Landau parameter $\kappa(0)$ and thermodynamic critical field $H_c(0)$ were calculated from $H_{c1}(0)$ and $H_{c2}(0)$. The values of $\xi(0)$, $\lambda(0)$ increase and $H_c(0)$ decrease gradually with the increasing of $x$. The values of $\kappa(0)$ is in the range of 7.9–9.4. The present results supported that La(Pt\textsubscript{1-x}Au\textsubscript{x})\textsubscript{4}Ge\textsubscript{12} system was a conventional type-II superconductor.

REFERENCES