

# **X-ray diffraction study on the thermal properties of CuMPt<sub>6</sub> (M=3d elements) alloys**

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## **Abstract**

The effect of ternary addition of the 3d elements Ti, V, Cr, Mn, Fe, Co and Ni to CuPt<sub>3</sub> to form ternary CuMPt<sub>6</sub> alloys on the thermal properties was investigated using high temperature X-ray diffraction method. Data obtained were utilized to determine the lattice parameters, coefficients of thermal expansion, Debye temperature and mean square displacements of an atom. It was found that the addition increases the lattice spacing, increases the degree of thermal expansion and lowers the Debye temperature. The results are discussed within the framework of the classical theory.

*Keywords* : CuMPt<sub>6</sub> alloys; X-ray diffraction; thermal expansion; Debye temperature

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## 1. Introduction

Platinum-based alloys have been an attractive subject of recent investigations in several fields, mainly due to increasing importance of their technological applications such as shape memory alloys [1], catalysts in hydrocarbon reforming and conversion [2] and electrocatalysts in fuel cells [3-6]. The alloy Cu-Pt is one of the typical Pt-based binary alloy systems with a phase of continuous solid solution in all proportions. At the composition CuPt<sub>3</sub>, it possesses a cubic ordered structure closely related to the Cu<sub>3</sub>Au-type one [7]. By adding 3d elements, designated here by the letter M, a series of ternary alloys CuMPt<sub>6</sub> were formed, which have shown a trend to form the Cu<sub>3</sub>Au-type ordered structure [8,9] similar to the binary MPt<sub>3</sub> alloys [10,11]. Thermal expansion is one of the fundamental physical properties for materials science and engineering. For Pt-based alloys, measurements of thermal expansion have hitherto been performed mainly for binary alloys which are mostly in disordered state.

In the present study, we have investigated the thermal properties of CuMPt<sub>6</sub> alloys with M = Ti, V, Cr, Mn, Fe, Co and Ni by using high temperature X-ray diffraction method. Information on the thermal expansion and the thermal vibration was obtained through the temperature dependence of the position and the intensity of Bragg reflections at elevated temperatures and is compared with that of CuPt<sub>3</sub> alloy. The effect of ternary addition on the thermal properties of CuMPt<sub>6</sub> is discussed.

## 2. Experimental procedures

Round shaped master ingots (~12 gram each) of the polycrystalline CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys were prepared from 99.999 % pure materials by conventional arc-melting under an argon gas atmosphere and by casting on a copper hearth. Each alloy was remelted twelve times to ensure the homogeneity. Chemical compositions determined by electron probe microanalysis were nearly the same as the stoichiometric ones. Thin slices were cut from the alloy ingots, grounded and polished to produce a smooth surface suitable for X-ray diffraction (XRD) measurements. The samples were encapsulated in quartz tubes under a vacuum of 10<sup>-4</sup> Pa and annealed at 1273 K for two days to homogenize the composition and remove strains. They were then furnace cooled to 873 K, annealed again at this temperature for three weeks and finally cooled to room temperature.

High temperature X-ray diffraction (HTXRD) experiments were performed on a two-circle X-ray diffractometer (Philips X'Pert Pro) equipped with a solid state detector (Philips, X'Celerator) and a high temperature attachment (Anton-Paar HTK-16).  $CuK_{\alpha}$  radiation was used, the voltage and current being 45 kV and 40 mA, respectively. Diffraction patterns were taken in the scattering angle range of  $20^{\circ}$  -  $140^{\circ}$  in step-scan mode under  $\theta-2\theta$  geometry with divergence and receiving slits of  $0.5^{\circ}$  in opening. HTXRD experiments were carried out in the temperature range of 300 – 773 K at an interval of 10 K with an accuracy of the temperature within  $\pm 1$ K. During the measurement, samples were kept in the evacuated chamber whose vacuum level was approximately  $10^{-4}$  Pa.

### 3. Results and interpretation

#### 3.1 X-ray diffraction patterns at room temperature

Figure 1 shows X-ray diffraction patterns of  $CuMPt_6$  and  $CuPt_3$  at room temperature. Sharp superlattice reflections at 100, 110, 210 etc. in the patterns of the  $CuMPt_6$  with  $M = Ti, V, Cr, Mn$  and  $Fe$  show that the alloys are in the ordered state of the  $Cu_3Au$ -type. Superlattice reflections are weak for  $CuCoPt_6$  and  $CuPt_3$ , indicating incomplete ordering. They are hardly observable for  $CuNiPt_6$ , indicating that much longer annealing is required for the attainment of ordering. Lattice parameter for each alloy was measured and is listed in Table 1. The results are consistent with the previous ones [9]. It is clearly shown that the addition of any of the 3d elements to  $CuPt_3$  increases lattice parameter. The increase is more pronounced in the alloys with smaller atomic number of M. It is particularly notable for  $CuMnPt_6$ , which can be attributed to the larger atomic size of Mn [13].

#### 3.2 Thermal expansion

Lattice parameter at various temperatures  $a(T)$  was determined by analyzing the peak position of a Bragg reflection at high scattering angle, whose temperature dependence is plotted in Fig. 2(a) for  $CuMPt_6$  and  $CuPt_3$ . The curves were fitted with the following equation;

$$a(T) = A + BT + CT^2, \quad (1)$$

where  $A$  is a temperature independent term and corresponds to the lattice parameter at absolute zero temperature.  $B$  and  $C$  represent the coefficients of the linear and quadratic terms of the temperature dependence, respectively. The values of  $A$ ,  $B$  and  $C$  are listed in Table 2. The coefficient of thermal expansion  $\alpha(T)$  as a function of temperature is obtained by taking differential of  $a(T)$ ,

$$\alpha(T) = \frac{1}{a(T)} \left( \frac{da(T)}{dT} \right) = \frac{1}{a(T)} (B + 2CT). \quad (2)$$

Temperature dependence of  $\alpha(T)$  is shown in Fig. 2(b) and its values at 300K and 773K are listed in Table 2. It can be seen that the addition of M to CuPt<sub>3</sub> gives rise to larger  $\alpha(T)$  value at 300 K.  $\alpha(T)$  increases almost linearly with increasing temperature, but there is no systematic dependence of the increase on the atomic number of M; the increase is relatively large for M=V and Mn, about 24% at 773K compared to that at 300K, and around 5% for M=Ti, Cr and Fe, while it is about 15 and 8% for M=Ni and Co, respectively. The increase for CuPt<sub>3</sub> is 38%. Relatively large values of  $C$  for CuPt<sub>3</sub> and CuMPt<sub>6</sub> with M=V and Mn, as shown in Table 2, indicate that the large temperature variation of  $\alpha(T)$  mainly comes from higher order of lattice anharmonicity.

It is to be noted that the  $\alpha(T)$  value of the CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys is an order of magnitude smaller than that of Pt-based alloys which is of the order of  $10^{-5} \text{ K}^{-1}$  [14].

### 3.3 Mean square displacement of an atom and Debye temperature

Mean square displacement of an atom and Debye temperature are determined from temperature variation of the integrated intensity of a fundamental reflection. The intensity of the reflection with the indices  $hkl$  of a polycrystalline sample is given, with multiplicity  $p$  and Lorentz-polarization factor  $LP$ , as

$$I_{hkl} = K p |F_T|^2 LP, \quad (3)$$

where  $F_T$  is the structure factor including temperature vibration of the constituent atoms, and  $K$  is a constant. For the fundamental reflection of CuMPt<sub>6</sub> alloy,  $F_T$  is expressed by

$$F_T = 4 \left( \frac{1}{8} f_{Cu} e^{-M_{Cu}} + \frac{1}{8} f_M e^{-M_M} + \frac{6}{8} f_{Pt} e^{-M_{Pt}} \right), \quad (4)$$

where  $f_i$  and  $e^{-M_i}$  are the scattering factor and Debye-Waller factor of atom  $i$ , respectively.  $M_i$  is given as

$$M_i = B_i(T) \frac{\sin^2 \theta}{\lambda^2}, \quad (5)$$

where  $B_i(T)$  is the temperature parameter of the atom  $i$ , and  $\lambda$  is the wavelength of the incident X-rays.

An approximation is made here that

$$\bar{B}(T) = B_{Cu}(T) = B_M(T) = B_{Pt}(T).$$

The integrated intensity is then written as

$$I_{hkl} = K p F^2 LP e^{(-2\bar{M})}, \quad (6)$$

with

$$F = 4 \left( \frac{1}{8} f_{Cu} + \frac{1}{8} f_M + \frac{6}{8} f_{Pt} \right) \quad (7)$$

and  $\bar{M} = \bar{B}(T) \frac{\sin^2 \theta}{\lambda^2}$ .

$\bar{B}(T)$  is, by definition, proportional to the mean square displacement of an atom  $\bar{u}^2(T)$ , which is given at high temperature in terms of the Debye temperature  $\Theta_D$ ;

$$\bar{B}(T) = 8\pi^2 \bar{u}^2(T) = \left( \frac{6h^2}{mk_B} \right) \left( \frac{T}{\Theta_D^2} \right), \quad (8)$$

where  $h$  is the Planck's constant,  $m$  is the average mass of the constituent atoms and  $k_B$  is the Boltzmann constant.

Rewriting eq. (6) as

$$\ln \left( \frac{I_{hkl}}{p F^2 LP} \right) = \ln K - \left[ 2\bar{B}(T) \frac{\sin^2 \theta}{\lambda^2} \right] \quad (9)$$

and plotting the left-side quantity against temperature, it is possible to determine  $\Theta_D$  through the relation (8). In this analysis high angle 311 reflection was used, for which the effect of thermal vibration is much pronounced. Correction was made for an anomalous dispersion effect for the atomic scattering factor using the values in reference [15]. Figure 3(a) shows a plot of  $\ln\left(\frac{I_{hkl}}{p F^2 LP}\right)$  against T for CuMPT<sub>6</sub> and CuPt<sub>3</sub> alloys in the temperature ranges between 300 and 773K.  $\Theta_D$  determined from the slope of the curves are listed in Table 3 and  $\overline{u^2}(T)$  is plotted as a function of temperature in Fig. 3(b). It can be seen that  $\overline{u^2}(T)$  of CuMPT<sub>6</sub> is larger than that of CuPt<sub>3</sub> in the whole range of temperature. As a result, the Debye temperature in Table 3 shows the highest value for CuPt<sub>3</sub>. The  $\Theta_D$  values for CuMPT<sub>6</sub> are classified in two groups: relatively high  $\Theta_D$  for M=V, Mn and Fe and relatively low  $\Theta_D$  for M = Ti, Cr, Co and Ni. In general, the temperature parameter  $B(T)$  contains both thermal and static components i.e.,  $B(T) = B_{thermal} + B_{static}$ . However, Fig. 3(b) shows that extrapolation of  $\overline{u^2}(T)$  curve of all the alloys goes to nearly zero value at the zero temperature, indicating that  $B_{static}$  is negligibly small.

The correlation between thermal expansion and thermal vibration amplitude suggested by Houska and Stein [17] for cubic materials does not hold for the CuMPT<sub>6</sub> alloys.

#### 4. Remarks

The present investigation has revealed that the addition of the 3d elements results in the larger lattice parameter, larger thermal expansion and larger mean square displacement of an atom for the CuMPT<sub>6</sub> alloys. In other words, the addition induces “static expansion” and “dynamic softening” of the crystal lattice. Replacing of Cu atoms with M atoms weakens interatomic bonding force.

Although there is some variation in the thermal properties among the CuMPT<sub>6</sub> and CuPt<sub>3</sub> alloys, they all have smaller coefficient of thermal expansion than that of Pt-based disordered alloys [14] and also than that of pure Pt metal [16]. This fact suggests a possible way of an application such that the thermal expansion can be depressed to a smaller degree by using alloys which have been heat-treated to develop long-range

atomic order. More extensive investigation of thermal properties in relation to atomic order in alloys is necessary for seeking a way to improve properties of materials in the field of thermo- engineering.

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### Figure captions

Fig. 1 Polycrystalline X-ray diffraction patterns of CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys at room temperature initially annealed at 873K.  $CuK_{\alpha}$  radiation was used.

Fig. 2: (a) Temperature dependence of lattice parameter of CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys. (b) Temperature dependence of the coefficients of thermal expansion of CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys.

Fig.3: (a) Plot of  $\ln\left(\frac{I_{311}}{p F^2 LP}\right)$  against temperature for CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys. (b) mean-square amplitude of thermal vibration of CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys plotted as a function of temperature.

### Table captions

Table 1: Lattice parameter of CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys at room temperature.

Table 2: Coefficients of thermal expansion at 300 and 773 K, and values of the coefficients  $A$ ,  $B$  and  $C$  of Eq. (1) obtained by fitting the curves in Fig. 2 (a).

Table 3: Debye temperature  $\Theta_D$  of CuMPt<sub>6</sub> and CuPt<sub>3</sub> alloys.

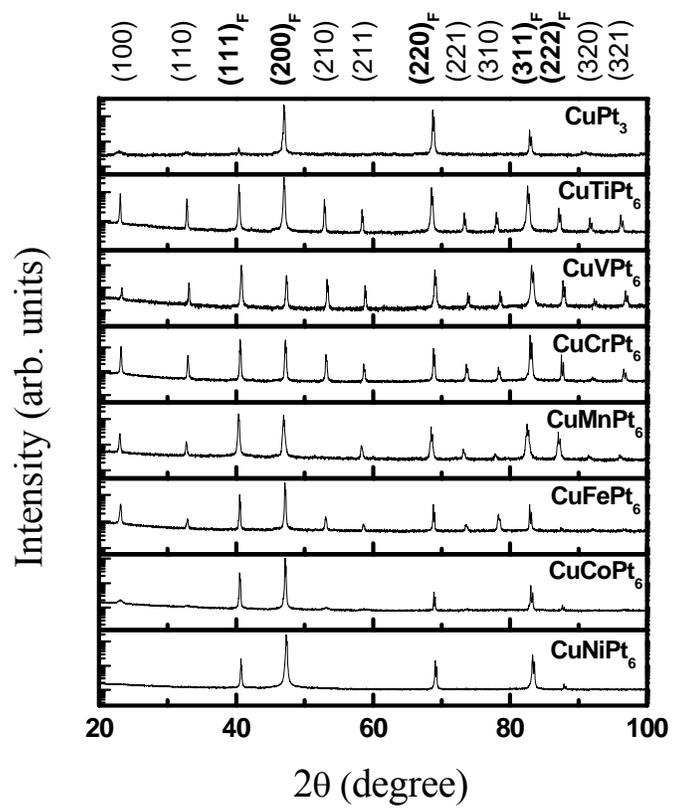


Figure 1

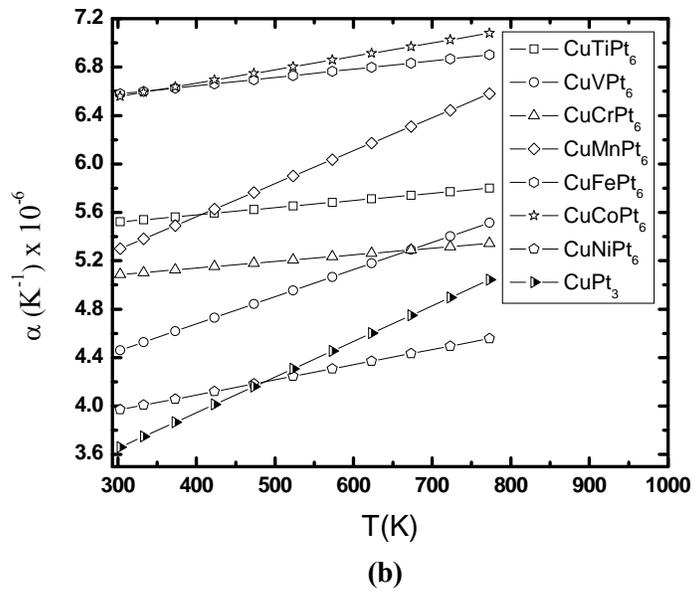
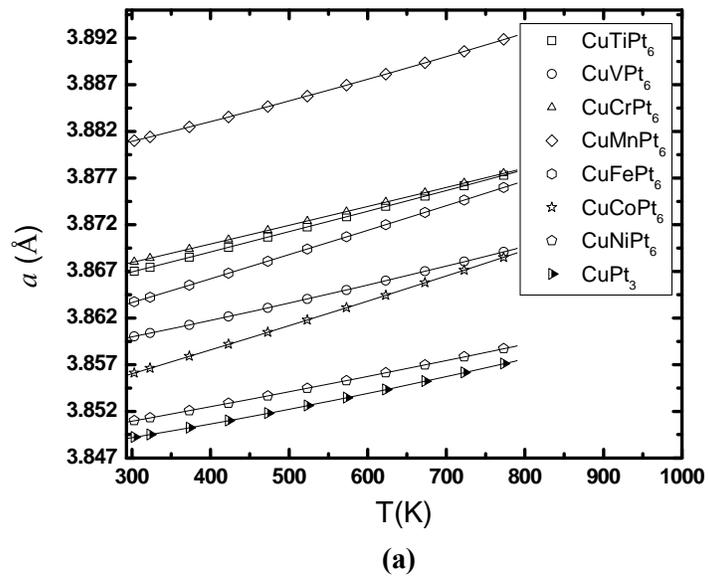
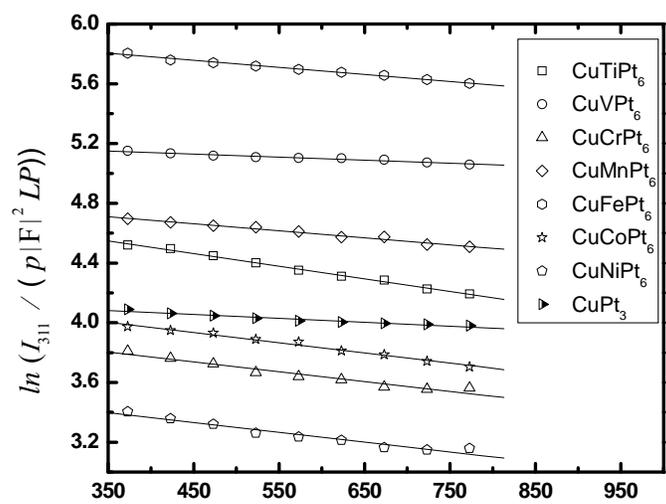
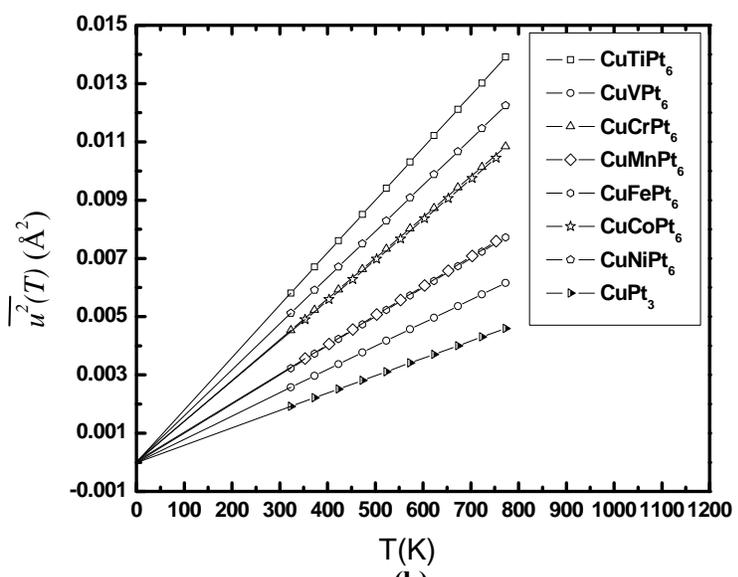


Figure 2



(a)



(b)

Figure 3

**Table 1**

Sample	Lattice parameter (Å)
CuPt <sub>3</sub>	3.849 ± 0.002
CuTiPt <sub>6</sub>	3.867 ± 0.001
CuVPt <sub>6</sub>	3.860 ± 0.003
CuCrPt <sub>6</sub>	3.868 ± 0.003
CuMnPt <sub>6</sub>	3.881 ± 0.002
CuFePt <sub>6</sub>	3.864 ± 0.002
CuCoPt <sub>6</sub>	3.856 ± 0.001
CuNiPt <sub>6</sub>	3.851 ± 0.002

**Table 2**

Sample	$\alpha(300\text{K}), \alpha(773\text{K})$ $\times 10^{-6} (\text{K}^{-1})$	A (Å)	B ( $\times 10^{-5}$ ) ( $\text{ÅK}^{-1}$ )	C ( $\times 10^{-9}$ ) ( $\text{Å K}^{-2}$ )
CuPt <sub>3</sub>	3.64 , 5.04	3.845	1.062	5.711
CuTiPt <sub>6</sub>	5.52 , 5.80	3.861	2.062	1.211
CuVPt <sub>6</sub>	4.45 , 5.51	3.855	1.456	4.384
CuCrPt <sub>6</sub>	5.08 , 5.34	3.862	1.900	1.111
CuMnPt <sub>6</sub>	5.29 , 6.58	3.875	1.731	5.365
CuFePt <sub>6</sub>	6.58 , 6.90	3.856	2.456	1.415
CuCoPt <sub>6</sub>	6.56 , 7.08	3.849	2.394	2.230
CuNiPt <sub>6</sub>	3.97 , 4.56	3.847	1.381	2.444

**Table 3**

Sample	$\Theta_D$ (K)
CuPt <sub>3</sub>	389 ± 5
CuTiPt <sub>6</sub>	225 ± 9
CuVPt <sub>6</sub>	337 ± 8
CuCrPt <sub>6</sub>	254 ± 4
CuMnPt <sub>6</sub>	300 ± 9
CuFePt <sub>6</sub>	301 ± 6
CuCoPt <sub>6</sub>	255 ± 8
CuNiPt <sub>6</sub>	239 ± 7