

# Structure and physical properties of ternary ordered phases CuMPt<sub>6</sub> with M=3d elements

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## Abstract

Measurements were made of in-situ X-ray diffraction, electrical resistivity and magnetic susceptibility for a series of newly found ternary alloys CuMPt<sub>6</sub> with M=Ti, V, Cr, Mn, Fe, Co and Ni. They possess, after appropriate heat treatment, the Cu<sub>3</sub>Au-type ordered structure, though the ordering is not complete for M=Ni. They are fairly good electrical conductor with a specific resistivity of around  $6 \times 10^{-3}$  ohm · m. A general trend has been found in the magnetic property: nonmagnetic – spin-glass-like – ferromagnetic – paramagnetic, with increasing atomic number of M.

The alloy with M=Mn, however, is specific among the seven alloys in that it undergoes secondary ordering into the cubic ABC<sub>6</sub>-type structure and is regarded as a counterpart of the Heusler alloy forming in the bcc systems.

*Keywords* : CuMPt<sub>6</sub> ternary alloys; Order-disorder transition; X-ray diffraction; Electrical resistivity

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## 1. Introduction

Extensive studies have been done in recent years to search new ordered phases in multi-component alloy systems. We have focused attention to alloys containing platinum, one of the  $5d$  elements having unique metallic character. In the binary alloy system, it forms a continuous solid solution with copper and, at the composition  $\text{CuPt}_3$ , an ordered phase appears with the less common orthorhombic structure [1, 2]. Platinum dissolves other  $3d$  elements, designated here by the letter M, to considerable extent and an ordered phase forms at the composition  $\text{MPt}_3$ , whose structure is, on the other hand, of the well-known  $\text{Cu}_3\text{Au}$ -type. It is of interest to see what kind of ordered structure appears when  $\text{CuPt}_3$  is combined with  $\text{MPt}_3$  to form a ternary alloy of the composition  $\text{CuMPt}_6$ .

Seven kinds of the ternary alloys with M ranging from Ti to Ni were prepared and their structural behaviour was investigated by X-ray and neutron diffraction methods [3, 4]. On annealing at temperatures below 873 K, ordering has occurred in the alloys with  $\text{M}=\text{Ti}$ , V, Cr, Mn, Fe and Co and the structure is of the  $\text{Cu}_3\text{Au}$ -type, though the ordering does not develop and the structure has remained to be face-centered cubic (fcc) for  $\text{M}=\text{Ni}$ . Detailed X-ray diffraction measurements on single crystals of the  $\text{CuMnPt}_6$  alloy have revealed that further ordering takes place and the structure changes from the  $\text{Cu}_3\text{Au}$ -type into the cubic  $\text{ABC}_6$ -type with a unit cell as large  $2\times 2\times 2$  as the fcc unit cells. The large unit cell is divided into three sublattices, A, B and C, and the atomic sites on the A and B sublattices are at the corner positions and those on the C sublattice are at the face-centered positions, as shown in Fig. 1. The structure is regarded as a layered one consisting of alternate (111) planes, one containing the A- and C-sublattice sites and the other containing the B- and C-sublattice sites. Alternatively, if the atoms on the C-sublattice sites are disregarded, it is the ordered structure of the NaCl-type consisting of the atoms on the A- and B-sublattices. The  $\text{ABC}_6$ -type structure is a new ordered structure forming in ternary fcc alloys.

In the present study, investigation has been done to find any dependence of electrical and magnetic properties of the ternary alloys on the atomic number of the M elements. The results of

measurements are reported in the following with those of further investigation on the ordering transition by in-situ X-ray diffraction method.

## 2. Experimental Procedures

Alloy specimens with the stoichiometric composition  $\text{CuMPt}_6$  (M=Ti, V, Cr, Mn, Fe, Co and Ni) were prepared by using conventional arc melting furnace in argon gas atmosphere, the starting materials being 99.9 or 99.99% pure. To attain homogeneity, each alloy ingot was re-melted 12 times by turning it over consecutively. Heat treatments were made by encapsulating the specimens in evacuated quartz tube at temperatures ranging from 1273 to 673 K for different periods of time. Chemical compositions of the alloy specimens were checked by an electron probe microanalyzer and deviation from the stoichiometry was less than 1.5 at%.

In-situ X-ray diffraction measurements for polycrystalline specimens were made employing a two-circle X-ray diffractometer (Philips, X'Pert Pro) equipped with a rapid counting system (X'Celerator) and a high temperature attachment (Anton Paar, HTK16), Cu  $K\alpha$  radiation being used.

Electrical resistivity measurements were made by the four-point probe method, where nano-volt meter (Keithley, 2182) and source meter (Keithley, 2400), controlled by the system Lab VIEW (National Instruments), were used. Magnetic susceptibility and magnetization measurements were carried out using a Superconducting Quantum Device (SQUID). Temperature variation of the magnetic susceptibility was measured in the temperature range between 5 and 300 K in the following way. At first, the sample was cooled down to 5 K in zero field, then the susceptibility was measured in the magnetic field of 0.01 T with raising temperature. After reaching the highest temperature, the sample was cooled down keeping the field at 0.01 T. The warming and cooling processes are denoted here as ZFC and FC, respectively. The field dependence of magnetization was also measured up to 5T at 5 K for alloys which show a ferromagnetic behaviour.

## 3. Results

X-ray diffraction patterns on polycrystalline specimens were taken at elevated temperatures both to identify the phase and determine the phase transition temperature. The transition temperatures from the fcc disordered phase to Cu<sub>3</sub>Au-type ordered phase is tabulated in Table 1. For the alloy with M=Mn, the transition temperature of the secondary ordering is also shown.

The lattice parameter values of the seven ternary alloys in the Cu<sub>3</sub>Au-type ordered state (except for M=Ni) measured at room temperature in our previous report [3] are plotted in Fig. 2. They are in the range 3.87-3.88 Å, but a marked deviation is seen for the alloy with M=Mn.

Temperature dependence of electrical resistivity is similar to that observed for ordinary metals. Values of the electrical resistivity of the seven alloys measured at room temperature (in the state of the Cu<sub>3</sub>Au-type order except for M=Ni) are listed in Table 1. They are in general 6 times larger than that of the platinum metal ( $1.06 \times 10^{-3} \Omega \text{m}$ ).

Temperature dependence of magnetic susceptibility for the alloys with M=Ti and V shows that they are nonmagnetic, although susceptibility increases gradually towards the lowest temperature of 5 K. Typical features of spin-glass, a cusp type anomaly and remanent magnetization, have been observed in the susceptibility of the alloys with M=Cr and Mn, as shown for M=Cr in Fig. 3. The freezing temperatures  $T_g$ , estimated from the cusp position, are 15 and 35 K for M=Cr and Mn, respectively. When the latter alloy is in the ABC<sub>6</sub>-type ordered state,  $T_g$  increases to 40 K.

Transformation to ferromagnetic order has been observed in the alloys with M=Fe and Co with Curie temperature  $T_C$  of 210 K for M=Fe and 190 K for M=Co, respectively.  $T_C$  of the latter is slightly dependent on the degree of order and decreases to 185 K when the long-range order vanishes. Magnetization curve of the two alloys shows little hysteresis and magnetic moment per one CuMPT<sub>6</sub> molecule estimated from the value of magnetization at 5T is  $4.1 \mu_B$  for M=Fe and  $2.8 \mu_B$  for M=Co. In Fig. 4(a) susceptibility is shown as a function of temperature and in Fig. 4(b) magnetization curve up to 5T is shown for M=Co in the Cu<sub>3</sub>Au-type ordered state. The alloy with M=Ni is paramagnetic down to 5K, and magnetic moment per one

CuNiPt<sub>6</sub> molecule estimated from the susceptibility above 100K is 2.8  $\mu_B$ .

Magnetic properties of the seven ternary alloys are summarized in Table 1. A general trend, nonmagnetic – spin-glass-like – ferromagnetic – paramagnetic, is seen with increasing atomic number of the M elements. This trend is similar to what has been observed for the Pt-rich Pt-M binary alloys [5].

#### 4. Discussion

In the ternary alloys CuMPt<sub>6</sub> formed by combining the binary phases CuPt<sub>3</sub> and MPt<sub>3</sub>, only the Cu<sub>3</sub>Au-type ordered structure forms (except for M=Ni) and the orthorhombic ordered structure does not appear. This is interpreted on the basis of the static concentration wave model [6, 7] as that the presence of the M element suppresses evolution of the L1<sub>1</sub>-type wave which leads to the formation of that structure and only L1<sub>2</sub>-type wave is active upon ordering.

The alloy with M=Mn undergoes, on further lowering temperature, transition into the ABC<sub>6</sub>-type ordered phase. The two step ordering was observed in the binary Pt-Mn alloys in our previous study [8] and it is no doubt that the coexistence of platinum and manganese is responsible for the unique ordering behaviour. There are no other fcc alloys in which ordering transition proceeds in the two step cubic – cubic – cubic sequence. In bcc alloys there is a well-known Heusler alloy Cu<sub>2</sub>MnAl, in which two step ordering transition preserving the lattice type occurs [9]. CuMnPt<sub>6</sub> is regarded as the counterpart of the Heusler alloy.

Among the seven ternary alloys investigated, CuMnPt<sub>6</sub> is specific not only in the ordering behaviour but also in the lattice parameter, as shown in Fig. 2. Abnormally larger lattice parameter has been seen in manganese oxides, selenide, telluride, arsenide, antimonide, etc. [10] and the finding in the present study furnishes another evidence of the specific nature of Mn. These facts suggest that this element gives rise in alloys and compounds to an interatomic interaction different from that of the other 3d elements. Study to investigate its origin is left as a future task.

The general trend observed in the M dependence of magnetic properties can be interpreted in terms of the behaviour of the

localized moment on the virtual band state formed by 3*d* electrons of the M elements, while M=Ti and V are nonmagnetic whose virtual levels are high above the Fermi energy. As the binary Pt-rich Pt-M alloys show similar M dependence for the magnetic properties, it is expected that an addition of the Cu atom has little effect on the virtual band state of M elements.

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## Figure captions

Fig. 1: Atomic arrangements of the  $ABC_6$ -type structure. A, B and C correspond to Cu, Mn and Pt atoms in  $CuMnPt_6$ , respectively.

Fig. 2: Lattice parameter of the  $CuMPt_6$  ( $M=Ti, V, Cr, Mn, Fe, Co$  and  $Ni$ ) alloys in the  $Cu_3Au$ -type ordered state (except for  $Ni$ , which is in the fcc disordered state).

Fig. 3: Temperature dependence of magnetic susceptibility for the alloy  $CuCrPt_6$  in the  $Cu_3Au$ -type ordered state, showing spin-glass like behaviour. ZFC and FC indicate that samples were cooled in zero field and in the field of 0.01T, respectively.

Fig. 4: Temperature dependence of magnetic susceptibility (a) and magnetization curve (b) of the alloy  $CuCoPt_6$  in the  $Cu_3Au$ -type ordered state.

Table caption

Table 1 : Structure, transition temperature, lattice parameter, electrical resistivity and magnetic behaviour of CuMPt<sub>6</sub> alloys.



Table 1

M in CuMPt <sub>6</sub>	Structural phases (transition temperature $T_c, T_{cl}$ )	Lattice parameter $\pm 0.001(\text{\AA})$	Electrical resistivity $\pm 0.1$ ( $10^{-3}\text{ohm} \cdot$ m)	Magnetic behaviour (freezing temperature $T_g$ or Curie temperature $T_C$ )
Ti	Cu <sub>3</sub> Au ( $T_c$ > 1573 K)	3.867	6.2	Nonmagnetic
V	Cu <sub>3</sub> Au ( $T_c$ > 1573 K)	3.860	6.6	Nonmagnetic
Cr	fcc	3.869	---	---
	Cu <sub>3</sub> Au ( $T_c =$ 1453) K)	3.868	5.9	Spin-glass-like ( $T_g = 15$ K)
Mn	fcc	3.884	---	---
	Cu <sub>3</sub> Au ( $T_c =$ 1241 K)	3.881	5.7	Spin-glass-like ( $T_g = 35$ K)
	ABC <sub>6</sub> ( $T_{cl} =$ 1019 K)	3.880	---	Spin-glass-like ( $T_g = 40$ K)
Fe	fcc	---	---	Ferromagnetic ( $T_C = 210$ K)
	Cu <sub>3</sub> Au ( $T_c$ = 1313 K)	3.864	5.8	Ferromagnetic ( $T_C = 185$ K)
Co	fcc	3.860	---	Ferromagnetic ( $T_C = 185$ K)
	Cu <sub>3</sub> Au ( $T_c$ = 1153 K)	3.856	5.7	Ferromagnetic ( $T_C = 190$ K)
Ni	fcc	3.851	5.5	Paramagnetic

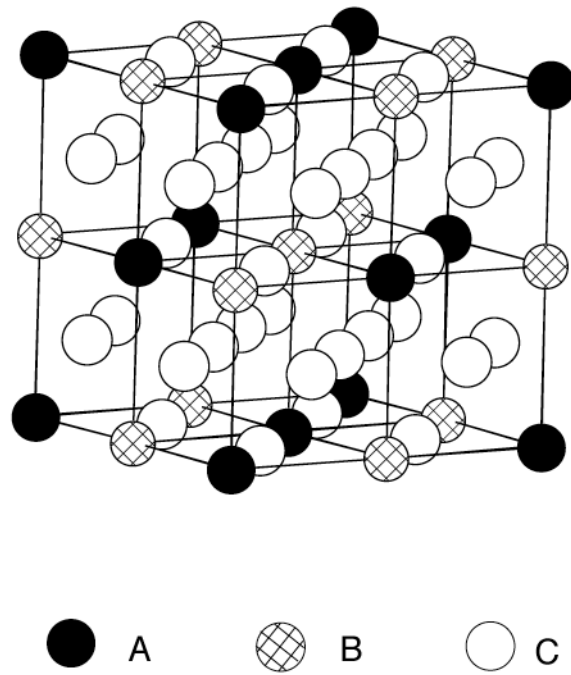


Fig. 1

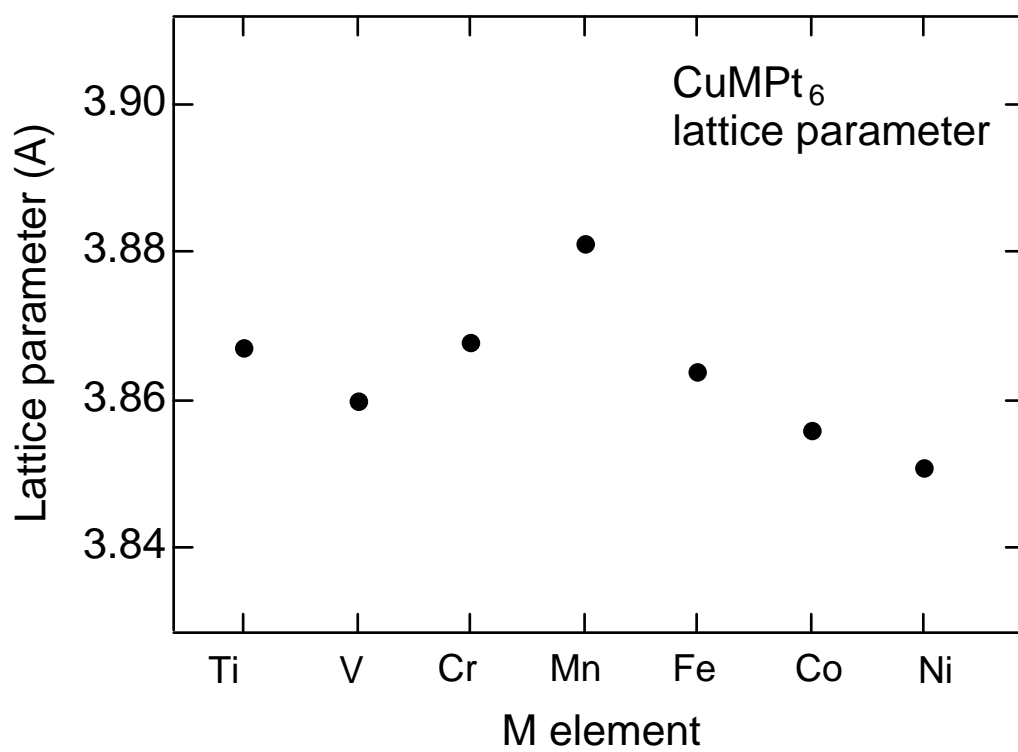


Fig.2

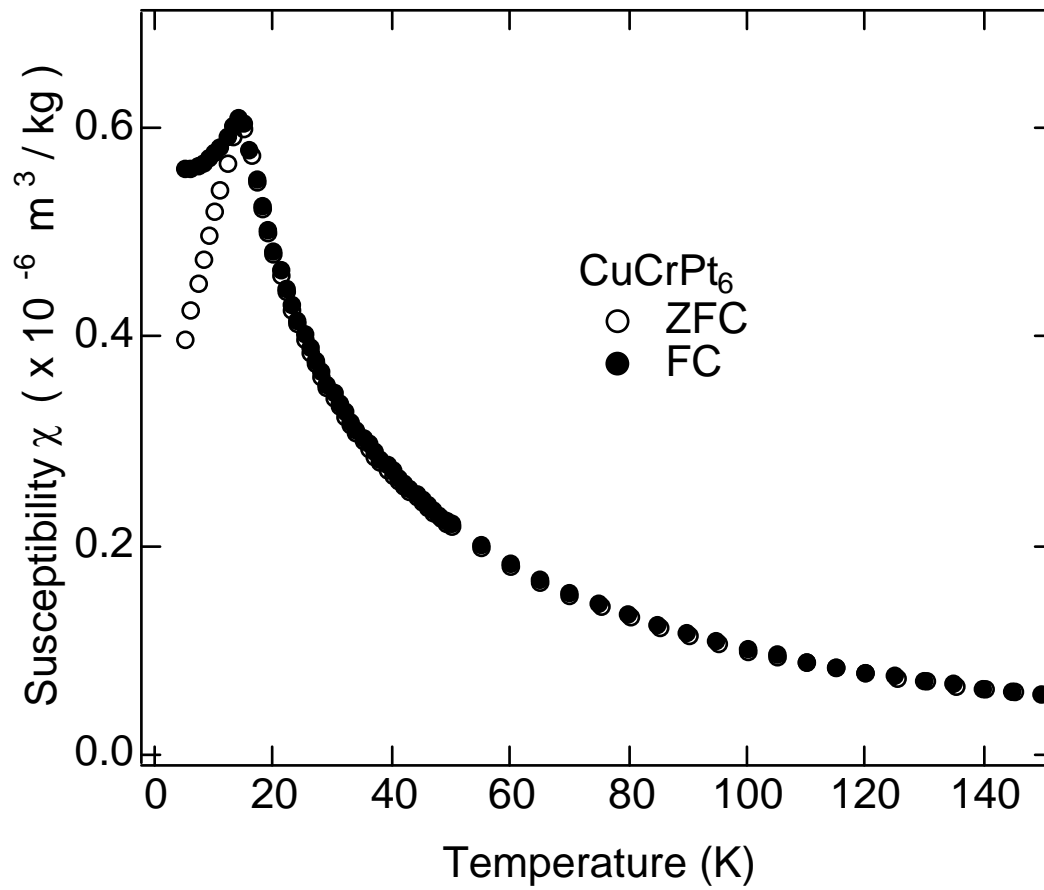
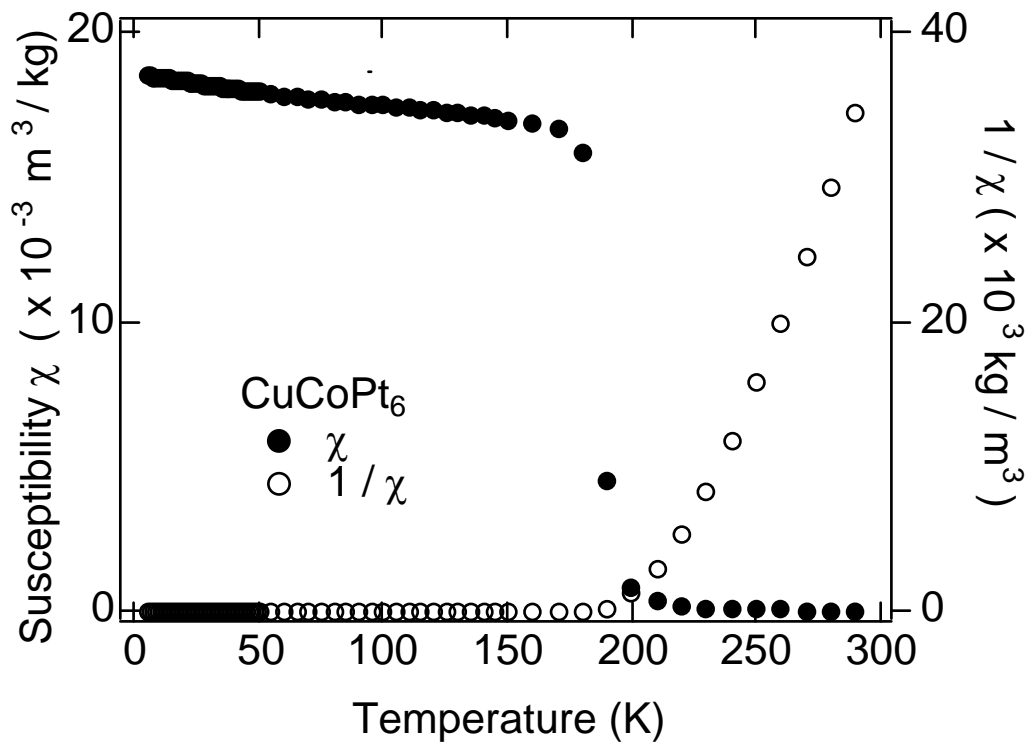


Fig.3

(a)



(b)

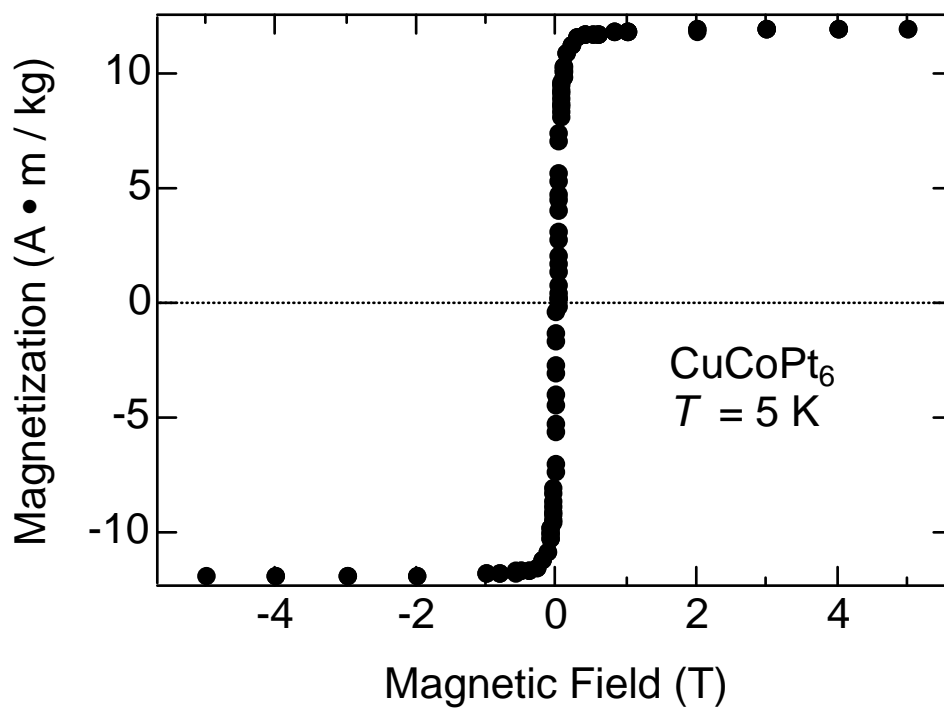


Fig. 4