

Lab 3 – MODULE β -1

ORDER-DISORDER TRANSITIONS

X-Ray Diffraction Study in CoPt System

OBJECTIVES

- Understand Order-Disorder Transitions
- Understand Factors affecting the Intensity of XRD peaks.
Calculation of Structure Factor “**F**”.
- Understand effect of Order-Disorder Transition on XRD pattern.
Superlattice - and fundamental lines.

SUMMARY of TASKS

- Sample preparation of CoPt equiatomic alloy at (25 to 925°C) temperature range.
- Obtain X-ray patterns of all samples using wide angle X-ray Diffraction (WAXD) technique.
- Calculate structure factor **F** for **ordered** (tetragonal) and **disordered** (FCC) phases of CoPt equiatomic alloy.
- Calculate order parameter “**S**” from (001) **superlattice** line and (111) **fundamental** line for all annealed samples.
- Plot “**S**” as a function of annealing temperature.
- Calculate critical temperature ‘**T_c**’ and exchanging energy ‘**V**’, based on Bragg-William’s equation.
- Calculate degree of tetragonality (**c/a**) for ordered tetragonal phase
- Calculate the average **particle size** of ordered phase, and plot it as a function of annealing temperature.

Material: CoPt equiatomic (50at.%) alloy.

INTRODUCTION

ORDER-DISORDER TRANSITIONS.

Lets consider for simplicity a binary alloy composed by two different types of atoms, A and B atoms. At high temperature (above a critical temperature T_c) A and B atoms are distributed in a random way occupying with the same probability any atomic site of the lattice. This state of the system is called the chemically disordered state. As temperature decreases, some degree of chemical ordering may occur, which means that A atoms prefer certain atomic sites, while B atoms occupy other locations in lattice. This rearrangement may be described as two distinct sublattices, one that is A-atom rich and the other B-atom rich, that penetrate each other. Such a structure is called a chemically ordered phase or superlattice. Usually ordering takes place at low temperatures, and for compositions given by AB or AB₃ formulas.

The degree of ordering for a certain binary system can be characterized by the order parameter S given by

$$S = (r_A - F_A) / (1 - F_A)$$

where r_A is the fraction of A lattice sites occupied by 'correct' atoms, i.e., A atoms, and F_A is the total fraction of A atoms in the system. There are two type of chemical ordering: **short-range**, which is characterized by a random distribution of two types of atoms (order parameter $S=0$), and **long-range**, with an order parameter different from zero.[1]

At absolute zero temperature the stable structure of a solid has the lowest enthalpy, or internal energy. As temperature increases, phase transitions often occur due to effects of entropy (less tightly bonded or more disordered structures). The competition between the effects of enthalpy (tendency of atoms to occupy regular positions) and entropy (opposing tendency of thermal agitation to maintain a random arrangement) determines if the system resides in the ordered or disordered state.

The presence of long-range and short-range order can be measured experimentally by their effects on X-ray, electron, and neutron scattering, as well as by their effects on some electrical, magnetic, thermal, and mechanical properties. On ordering, changes in atom distributions show very little effect on cell size, thus no changes in X-ray peak positions occur; however, peak intensity is strongly influenced. Calculation of X-ray peak

intensity, via the structure factor “**F**”, can be used as a tool to analyze each atomic arrangement.

On ordering, some extra diffraction reflections occur; these are called **superlattice lines**. Their presence in the X-ray pattern of the system shows that a change in Bravais lattice takes place in the chemically ordered state. Other type of lines, called **fundamental lines**, are present in both the ordered and disordered states, and show up at the same positions. In general, the superlattice lines are of much lower in intensity than fundamental lines.

CoPt System

Equimolar CoPt is a ferromagnetic alloy that exhibits chemical ordering. In the disordered state, CoPt exhibits a face-centered-cubic (FCC) structure with a random distribution of Co and Pt atoms in corner positions and face centers, as is shown in Fig.1a [2]. This high temperature structure exhibits weak magnetic anisotropy, which limits its use as a permanent magnet. At temperatures below 825°C this alloy orders into a tetragonal cell composed by alternate (001) atomic planes containing only Co or only Pt atoms. A similar superlattice occurs in other systems such as CuAu.[2,3] In this structure, each atom has 8 nearest neighbors of the opposite kind in adjacent (001) planes and four atoms of the same kind in its own (001) plane as is shown in Fig.1b [2].

The origin of the tetragonal distortion can be explain in terms of a more compression of the c-axis of the original FCC unit cell upon ordering, resulting in a Bravais lattice that is tetragonal, with a (c/a) ratio of about 0.973. The ordered tetragonal phase exhibits a high uniaxial magnetic anisotropy with its easy magnetization direction along the c-axis.

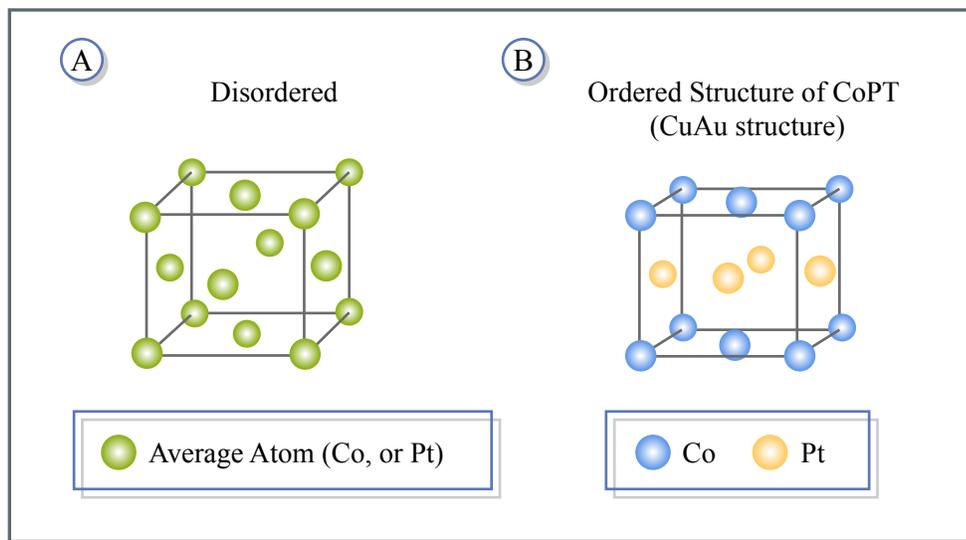


Figure by MIT OCW.

Fig.1 CoPt disordered and ordered phases. [2]

The **coercivity** in CoPt alloys strongly depends on how this alloy is heat treated. The coercivity is highest when equiatomic CoPt alloys are aged at temperatures well below the critical point (the order-disorder transition temperature), but high enough to provide atomic mobility. The optimum annealing temperature has been shown to be around 680°C.[4] The magnetic properties of CoPt make it a potentially interesting material from a commercial standpoint. Recently, thin films of ordered CoPt have been grown by the molecular beam epitaxy for magnetic recording and magneto-optical recording media applications.[5, 6, 7]

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INTENSITY OF X-RAY REFLECTIONS.

Factors governing Intensity of X-ray Reflections.

The measured intensities of X-ray reflections in a powder XRD pattern depend on six factors: 1) polarization factor, 2) structure factor, 3) multiplicity factor, 4) Lorentz factor, 5) absorption factor and 6) temperature factor. These factors will be discussed and analyzed in class.

Reading material

1. B. D. Cullity and S. R. Stock in “*Elements of X-ray diffraction*”, 3th edit., Prentice Hall, 2001, Chapter 4, pp. 123-157.
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3. C. Barret and T. B. Massalski in “*Structure of Metals*”, International Series on Materials Science and technology, Vol. 35, 1987 Chap. 11, pp.270-277.
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5. L. Uba, S.Uba, O. Horpynyuk, V. N. Antonov, A. N. Yaresko in “*Influence of the crystal structure and chemical order on the magnetic and magneto-optical properties of equiatomic CoPt alloy*”, Journal of Applied Physics, Vol. 91, Number 2, 2002, pp.775-779.
6. Q. F. Xiao, E. Bruck, Z. D. Zhang, F. R. de Boer, K. H. J. Buschow in “*Remenance enhancement and coercivity in two-phase CoPt bulk magnets*”, Journal of Applied Physics, Vol. 91, Number 1, 2002, pp. 304-307.
7. S. Uba, L.Uba, A. N. Yaresko, and A. Ya. Perlov in “Optical and magneto-optical properties of Co/Pt multilayers, Physical Rewiew, B,1996, pp.6526-6535.