Lab 4 – MODULE γ-2

ORDER-DISORDER TRANSITIONS

X-Ray Diffraction Study of Ordering in CoPt System

OBJECTIVES
● Understand Order-Disorder Transition.
● Factors affect the Intensity of XRD peaks.
 Calculation of Structure Factor "**F**".
● Effect of Order-Disorder Transition on XRD pattern.
 Superlattice vs. fundamental lines.

SUMMARY of TASKS
● Sample preparation of CoPt equiatomic alloy at (25 to 925∘C) temperature
 range.
● Obtain X-ray patterns using:
 --Wide Angle X-ray Diffraction(WAXD) at room temperature, and
 --"in situ" XRD measurements
● Calculate structure factor for **ordered (**tetragonal), and
 disordered (face centered cubic**)** 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 **'Tc'** 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.
Let consider for simplicity a binary system composed by two different types
of atoms, A and B atoms. At high temperature (above a critical temperature
Tc) A and B atoms are distributed in a random way occupying with the same
probability any atomic site of lattice. This state of system is called the
chemically **disordered state**.

 As temperature decreases some degree of chemical ordering occurs which
means that A atoms prefer certain atomic site, while B atoms occupy some
others locations in lattice. This rearrangement may be described as two
distinguished sublattices, one of A-atom reach and the other with B-atom
reach penetrate each other. Such a structure is called a chemically **ordered**
phase , or **superlattice**. When this arrangement of A and B atoms is set over
large distances it is called **long-range order**. Usually ordering takes place at
low temperatures, and for compositions given by AB or AB_3 formulas.

Order parameter "S"
Systems that exhibit order-disorder transition may exist in intermediate
states where the degree of ordering is not complete.
 Degree of ordering for a certain binary system can be characterized by order
parameter S defined as

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

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.
S=1 for perfect chemical order(r_A=1), and S=0 for complete disorder. For
partial order, $0 < S < 1$, the intensity of the superlattice reflections is less
than for S=1.

There are two types 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] Usually ordering takes place at relatively low temperatures and for
compositions given by AB or AB3 formulas.
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.

Effect of order-disorder transition on X-ray Diffraction pattern.
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, thermal and mechanical properties. On ordering, changes in atom distributions 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 structure factor "**F**", can be used as a tool to analyze each atom arrangement.

On ordering some extra diffraction reflections occurs; they are called **superlattice lines.** Their presence in the X-ray pattern of the system show that a change in Bravais lattice takes place in the chemically ordered state. Other type of lines, called **fundamental lines** are present in both 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.
The order parameter may be determined experimentally from the ratio of a superlattice peak intensity to that of a nearby fundamental line:

$$S = \sqrt{[(m_f\, LP_f) / (m_s\, LP_s)]} * (F_f / F_s) * \sqrt{(I_s / I_f)} \quad (2)$$

where the **m_i** are the multiplicity and **LP_i** the Lorentz polarization factors of the reflection of interest. The **I_i** are the measured intensities of the respective lines.
The Bragg-Williams theory provides expressions relating the chemical order parameter, S, and the ordering temperature, Tc, to the chemical ordering energy, V, that stabilizes the atomic –scale, ordered state.
Near the critical temperature:
$$S^2 = 3(Tc - T)/Tc \quad (3)$$

and
$$V_o = 4k_B Tc \quad (4)$$
Eq.3 allows to determine the Tc from the experimental temperature dependence of the order parameter near the critical temperature. Eq.4 then gives the chemical ordering energy from the ordering temperature.

CoPt System

Equiatomic 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 a weak magnetic anisotropy, which limits its use as a permanent magnet.
At temperatures below 825C 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 as CuAuI.[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.1,b[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.

A

Disordered

B

Ordered Structure of CoPT
(CuAu structure)

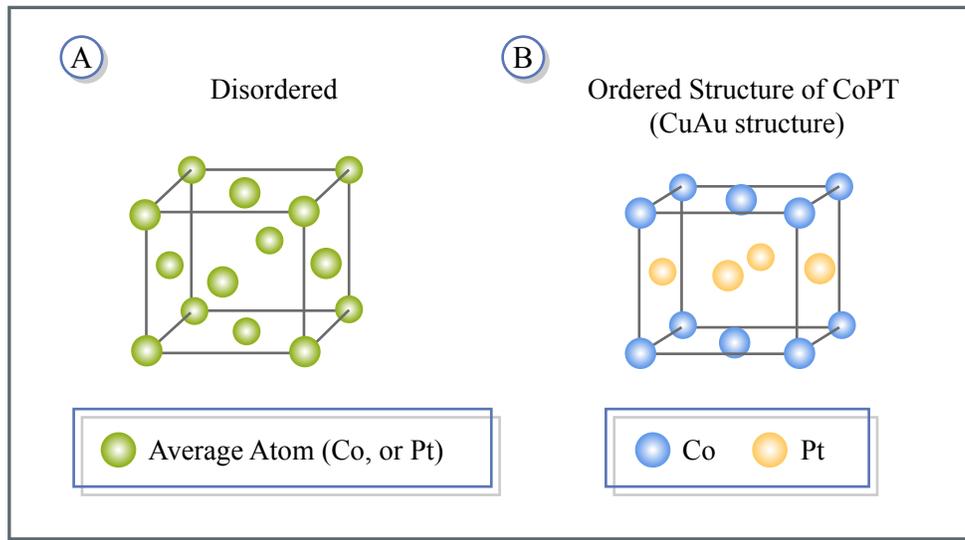Average Atom (Co, or Pt)

Co   Pt

Figure by MIT OCW.

Fig.1(a,b)

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 alloy 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]

INTENSITY OF X-RAY REFLECTIONS.

Factors governing Intensity of X-ray Reflections.
The measured intensities of X-ray reflections from polycrystalline samples depends on following factors:1)polarization factor, 2)structure factor, 3)multiplicity factor, 4)Lorentz factor, 5)temperature factor, and 6)absorption factor.
General formula for measured relative intensity is given by

$$I = I_{0*} |F|^{2*} p* [(1 + \cos^2 \theta) / (\sin^2\theta \cos \theta)]* e^{-2M} *A(\theta) \qquad (5)$$

where **I** is relative integrated intensity,
I_0 = incident intensity of X-ray beam,
F= structure factor,
θ =Bragg's angle,
A= absoption factor,
p=multiplicity factor,
e^{-2M} = temperature factor, and
$[(1 + \cos^2 2\theta) / (\sin^2\theta \cos \theta)]$ is Lorentz polarization factor

The X-ray intensity, I, scattered from a *point charge*, as a free electron, depends on incident intensity, I_0, distance, R from the sample, and X-ray polarization according to the Thompson equation,
$$I = (I_0 / R2)(1 + \cos^2 2\theta) / 2 \qquad (6)$$

where **2θ** is the angle between the direction of incident and scattered radiation (**θ** corresponds to the diffraction angle in Bragg's law:
  2d sin **θ = n λ**   where d is d-spacing, and λ is the wavelength of incident X-ray beam).
The factor **(1 + cos² 2θ)/2** is called *polarization factor*

It is easier to analyze the measured intensities step by step considering first X-ray scattering by a **single** electron, then by an **atom**, and finally by **all the atoms** of a unit cell.

Scattering by an atom. Atomic scattering factor "f"
The contribution of an atom in scattering X-rays is expressed by the **atomic scattering factor, "f"** which is defined as the *ratio of the amplitude of the wave scattered by the atom to that scattered by an electron under the same conditions*.
The atomic scattering factor is directly related to the distribution of electrons in atom. If atoms were point charge, f = Z. But electronic charge density is distributed over atomic volume. Hence, scattering from charge in different parts of atoms will have a phase difference that depends on scattering direction. (f=Z at $\theta = 0$ direction, and decreases with increasing θ-angle).[3]
Atomic scattering factor must appear in the scattered amplitude and f2 in the scattered intensity

Scattering from a Unit Cell. Structure factor "F"
What about the content of the unit cell, that is, which atoms are at which positions in the unit cell? That is determined by the structure factor.

Each atom in a unit cell scatters with an amplitude proportional to atomic scattering factor "**f**" for that atom at the corresponding angle **θ_{hkl}** , and with a certain phase dependent on its position in the unit cell.
The summation of the waves scattered by each of the atoms in the unit cell gives the resultant amplitude which is called the structure factor, **F.**
The intensity of the observed (hkl) reflection is proportional to the square of the absolute value of this resultant amplitude $\approx |F|^2$. For crystals possessed a center of symmetry, the structure factor is given by

$$|F|^2 = [\ \sum_j f_j \cos 2\pi (hx_j + ky_j + lz_j)\ ]^2 \quad (7)$$

where (hkl) are Miller indices for X-ray reflection, $x_j\ y_j\ z_j$ are coordinates of j-atom, and "**fj**" is the atomic factor of **j**-atom in unit cell.

Lorentz-polarization factor.
Real crystals are not perfect in most of the cases (they reflect over varying orientation ranges), and the X-ray incident beam is perfect parallel and monochromatic. Other factors related with the geometry also affect the relative intensity of X-ray reflection.
The contribution of all these factors in intensity is given by
Lorentz factor $= 1/(4\sin^2\theta \cos\theta)$ **(8)**

Lorentz-polarization factor , defined as

LP $= (1 + \cos^2\theta)/(\sin^2\theta \cos\theta)$ is a combination of equations (6)and (8).

Each X-ray diffraction method requires its particular form of Lorentz-polarization factor due to particular geometry. Values of this factor usually are tabulated as a function of θ-angle, and for our experiments we will use Tables of [3].

The Multiplicity Factor "p".
In the powder method all planes of the same d-spacing superimpose to the same diffraction cone. The multiplicity factor is given by the number of permutations of hkl indices that give the same $\sin^2\theta$ values in the quadratic form for the crystal[1].
In powder patterns of cubic crystals, which have high symmetry, p=6 for{100} planes, 8 for{111} planes, 12 for {110}, 24 for {hk0} and for {hhl}planes , and 48 for {hkl}.

The Temperature Factor e^{-2M}
Atoms in a crystal at a given temperature oscillate about their mean position. This deviation affects atomic scattering factor **f**. The higher the temperature the more **f** decreases as the diffraction angle is increased.
If each atom is assumed to vibrate independently of the others with a mean-square displacement U^2 at Bragg's angles to the (hkl) plane, the scattering factor will be reduced from **f** to $f(e^{-M})$ where
$$M = 8\pi^2 U^2 (\sin\theta)^2 / \lambda   \textbf{(9)}$$

The value of **M** may be different for each atom, and is anisotropic if the atom vibrates anisotropically. Assuming isotropic displacements (i.e all atoms of one type in a crystal vibrate equally), factor e^{-M} is almost equal for each of atoms, and F^2 becomes simply ($F^2 * e^{-2M}$)

The Absorption Factor, "A"

Absorption factor **A(θ)** describes the loss of intensity of the incident and reflected X-ray beam within the crystal. In some cases the absorption factor A, is given by a simple function of the *absorption coefficient* **μ,** but in general, for various of crystal and powder-sample shapes calculation of **A** is more complex.

If the crystal is thick enough to absorb all the initial beam, and if the reflective planes are parallel to the surface, absorption factor is simply given by

$$A = 1/2 \, \mu \quad (10)$$

Reading material

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