Ferromagnetic Transitions

Module γ-3: Phase Transitions and Magnetic Properties

Jorge Feuchtwanger

Objectives:

1. understand the *chemical order-disorder transition* and how it alters magnetic properties,
2. appreciate how a *first-order structural phase transformation* (in a ferromagnet) may affect magnetic properties,
3. understand the magnetic and thermal effects associate with the *ferromagnetic/paramagnetic transition* at the Curie temperature.

Summary of tasks:

1) Measure M-H curves for polycrystalline CoPt alloys quenched from various temperatures (300-900°C). Plot H_c and anisotropy field vs. quench temperature.

   Lessons to be learned: The chemical order/disorder transition in CoPt is second-order and brings with it a significant change in crystal symmetry. The decrease in crystal symmetry accompanying ordering brings with it an increase in magnetic anisotropy: a larger applied field is needed to saturate the ordered sample and the coercivity also increases.

2) (if time permits) Measure $M(T)$ in Ni-Mn-Ga crystal on increasing and decreasing temperature between 20 and 120°C at 200 Oe and 10 kOe.

   Lessons to be learned: The Curie temperature defines a second-order magnetic transition; the other transition observed is a first-order structural transformation between martensite and austenite. The latter shows up in the susceptibility because of the change in magnetic anisotropy that occurs with the change in crystal symmetry.

Materials needed

Ni-Mn-Ga powder, suitable for VSM measurements. $T_m \approx 30 - 60$°C, $T_C \approx 80 - 90$°C. Series of CoPt alloys quenched from different temperatures.

Equipment to be used

Vibrating sample magnetometer (VSM), Rm. 4-055

Background

Ni-Mn-Ga:

Ni_2MnGa is a member of a series of Heusler alloys (related to the DO_3 intermetallic compound Fe_3Al) having interesting electrical, magnetic, thermal and optical properties. Alloys of Ni-Mn-Ga close to the intermetallic compound Ni_2MnGa are chemically ordered below about 800°C in the $L2_1$ ordering (*Strukturbericht* notation, http://cst-www.nrl.navy.mil/lattice/struk/), with *Fm3m* symmetry, as pictured in Fig. 1. Phases close to the stoichiometric compound are ferromagnetic with a Curie temperature of about 80°C. They also have a structural transformation from a high-temperature cubic phase (austenite) to a low-temperature tetragonal phase (martensite); this transformation temperature falls between about 30 and 70°C. In the cubic state Ni-Mn-Ga has low coercivity and an almost-reversible *M-H* curve that saturates in a relatively-small applied field. In the tetragonal phase, there is a significant hysteresis and a larger field is required to saturate the magnetization.

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The term *martensitic transformation* applied originally to the structural change that occurs between α-Fe (BCC) and its metastable, carbon-containing, tetragonal phase, *martensite*. The term has since come to describe *any structural* transformation that occurs *without diffusion* and by means of a local atomic displacement. On cooling below the *martensite temperature*, the structure undergoes a first-order transformation that contracts one of the cubic axes and enlarges the other two. The low-temperature phase is body centered tetragonal with *I*4/*mmm* symmetry (it is rotated

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about the contracted c axis by 45° relative to the parent phase and has $a = b = 0.707 \times$ the lattice constant of the parent).

(Martensitic Ni-Mn-Ga alloys can be highly twinned. They are technically important because application of a magnetic field to the martensitic phase can give rise to strains of 6% through field-induced motion of twin boundaries.)

CoPt

CoPt is a ferromagnetic intermetallic compound that shows very strong dependence of its magnetic properties depending on its crystal structure. Below about 825°C, alloys close to the equiatomic compound, CoPt, order chemically (Fig. 2). The structure of chemically-*disordered* CoPt is FCC (Fig. 3, left). In the *ordered* state CoPt has alternate (001) planes fully occupied by Co with Pt planes in between (Fig. 3, center). The chemically-ordered phase contracts along the [001] direction making the Bravais lattice tetragonal with a c/a ratio of about 0.9x. (Fig. 3).   Note that the primitive lattice must be redefined by a 45° rotation about the c axis; it is now BCT.

Figure removed for copyright reasons.
Co-Pt phase diagram. From Baker, H., ed. *ASM Handbook Alloy Phase Diagrams*. Vol. 3. 10th ed. Materials Park, OH: ASM International, 1992. ISBN: 0871703815.

So, while the chemically ordered and disordered states are both crystalline, they have a different crystal structure, i.e. a different Bravais lattice and a different basis unit.
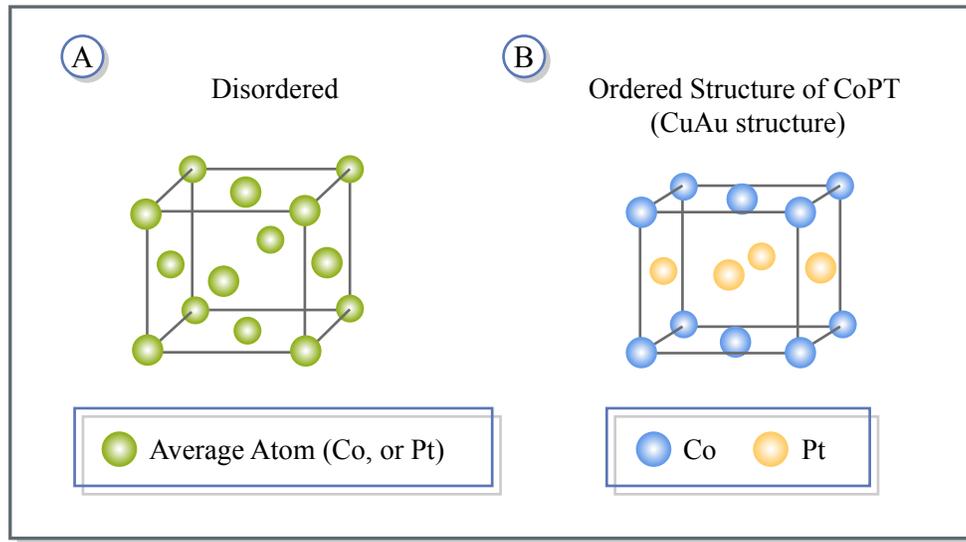

Figure by MIT OCW.

Fig. 3. Structures of disordered (left) and ordered CoPt.

There is an important difference between the chemical ordering and structural distortion in these two systems, Ni-Mn-Ga and CoPt. In CoPt, once the chemical ordering defines a unique axis (perpendicular to the alternating planes, Fig. 2), the *c*-axis contraction occurs simultaneously in the direction normal to those planes. The chemical ordering and symmetry lowering occur at the same temperature, they are part of the same transformation. In Ni-Mn-Ga, the chemical ordering occurs at about 800^oC but the tetragonal distortion does not occur until the temperature is less than about 100^oC. There is nothing in the symmetry of the chemical ordering (Fig. 1) that demands that the tetragonal distortion (at much lower temperatures) should occur along any particular <100> direction (unlike the ordering in CoPt). In fact, on cooling a Ni-Mn-Ga single crystal through the martensitic transformation, three equivalent variants of the tetragonal phase may nucleate, each having its tetragonal *c* axis parallel to either [100], [010], or [001]. The distribution of these three variants occurs to minimize elastic energy stored in the low-temperature phase.

Measuring *M-H*:

The *M-H* curves are measured with a vibrating sample magnetometer (VSM).

There are many instruments that can measure magnetization of a material. Most of them make use of Faraday's law of induction:

$$\oint E \cdot dl = -\frac{\partial}{\partial t} \oint B \cdot dA = -\frac{\partial \phi}{\partial t} \qquad (1)$$

It says that a voltage, $\oint E \cdot dl$, is generated in a path that encloses a time-changing magnetic flux, $\partial \phi / \partial t$. The sense of the voltage is consistent with Lenz's law as shown in Fig. 4.

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Fig. 4 A decrease in flux through a coil results in a voltage in that coil whose sense is such that its current would create a field opposing the initial change. (Courtesy of R. C. O'Handley)
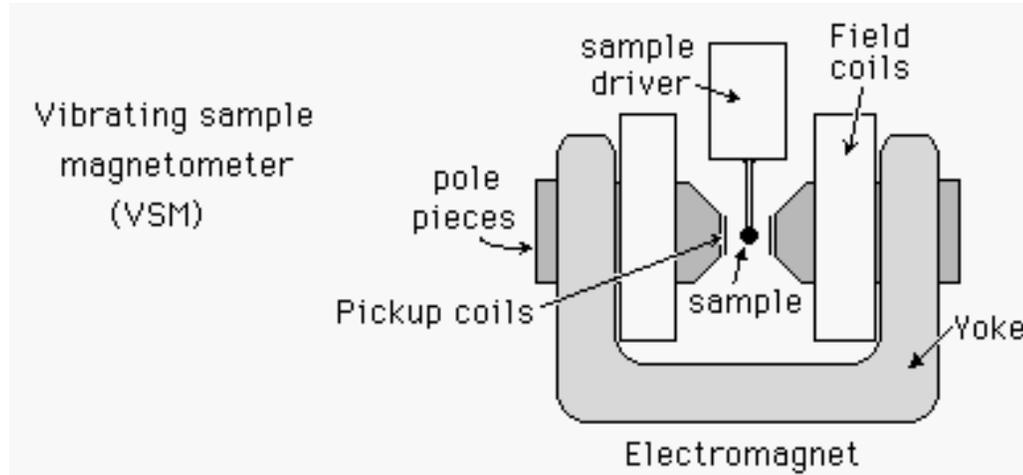
The *flux density* or magnetic induction inside a sample depends on the applied field and the sample magnetization, $B = \phi / A = \mu_o(H+M)$. Outside the sample ($M = 0$) the induction, $B = \mu_o H$, comes from the applied field and the H field due to the dipole moment of the sample. When the flux density around a magnetic sample is changed (by either moving the sample or the pickup coil, or by varying the sample magnetization with a small AC field), a voltage is induced in a nearby pickup coil. Integration of that voltage with time gives the flux change due to the sample.

The sample may be magnetized by an electromagnet, which generates a magnetic field by passing a current through a copper coil as shown in Fig. 5 and 6.

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Fig. 5. Direction of magnetic *B* field about a current-carrying solenoid is given by the right-hand rule (Courtesy of R. C. O'Handley).

We will use a vibrating sample magnetometer in which a sample is vibrated (± 1 mm at about 75 Hz) to induce a voltage in a set of carefully designed pickup coils. The sample is magnetized by the field of the electromagnet. The magnetic flux forms a circuit through the magnet yoke; the sample sits in an open part of that magnetic circuit as shown in Fig. 6.

Courtesy of R. C. O'Handley. Used with permission.

Fig. 6. Schematic of a vibrating sample magnetometer in which a sample is driven orthogonal to the field of an electromagnet. A set of pickup coils attached to the faces of the pole pieces of the electromagnet detects the magnitude of the magnetic moment of the oscillating sample. (Courtesy of R. C. O'Handley)

The signal generated in the pickup coils of the VSM depends on several factors:

1. the number of *turns* in each coil as well as the *coil orientation* and geometry,

2. the *amplitude* and *frequency* of the sample vibration, and

3. the *magnitude* of the magnetic moment, *MV,* of the sample.

Factors 1 and 2 are *instrumental* parameters that can be accounted for by calibration. The size of the magnetic moment depends upon the sample volume and its magnetization density, which in turn is a function of field and temperature. Hence the VSM signal depends on the state of magnetization of the sample, *M,* through *H* and *T.*   The VSM output is a plot of *M* vs. *H* at constant temperature or *M* vs. *T* at constant field.

Overview of magnetic properties

Magnetic materials derive their importance and usefulness from the fact that they have a property called the magnetization, $\boldsymbol{M} = N\boldsymbol{\mu_m}/V$ i.e. $\boldsymbol{M}$ is the volume density of atomic magnetic moments, $\boldsymbol{\mu_m}$. The magnetization can be changed by application of a magnetic field, $\boldsymbol{H}$. Applying a field tends to line up the magnetization with the field. The sum of the
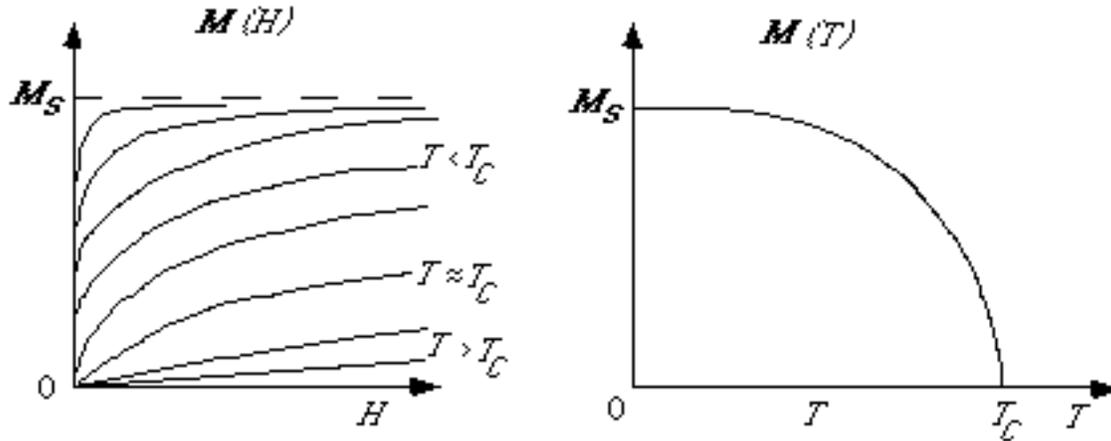
magnetization and the H field defines the flux density, B: $B = \mu_o(H + M)$ (mks) or $B = H + 4\pi M$ (cgs).

Units:	cgs		MKS	
Applied field:	H	(Oersted)	H	(Amperes /m)
Magnetic response:	M	(emu/cm^3)	M	(Amperes /m),
	or $4\pi M$	(Gauss)	$\mu_o M$	(Tesla)
Total flux density:	$B = H + 4\pi M$	(Gauss)	$B = \mu_o(H + M)$	(Tesla)

The properties of magnetic materials can be grouped into two categories, *fundamental* and *technical*. The fundamental properties are determined mainly by the electronic structure of the material, which in turn is a function of the *short-range order*, i.e. the number, type (chemistry), distance and symmetry of the nearest neighbors about a given atom. These include the saturation magnetization, M_s, the Curie temperature, T_C, (the temperature above which thermal energy destroys magnetic long-range order and, therefore, $M = 0$). [Other properties such as those associated with the *B-H* loop, e.g. the permeability, μ_r, the coercivity, H_c, and the remanent flux density, B_r, are of more technical importance. The technical properties are strongly dependent on microstructure (grain boundaries, texture, defects etc.) which in turn is predominantly a result of processing.] Fundamental properties are mainly a reflection of the thermodynamics of the material; technical properties reflect more the kinetics of the processing route by which the particular sample was made.

Fundamental properties

As temperature increases it becomes increasingly more difficult for the atomic magnetic moments in a material to maintain their alignment with each other or for an applied field to orient the atomic moments. The net spontaneous magnetization, vanishes at the Curie temperature, T_C (Fig. 7). Above T_C, atomic magnetic moments may still exist but their long-range orientations are no longer correlated. Of course, with a strong enough field, one could overcome the effects of $k_B T$ and fully align these paramagnetic moments, but at room temperature such fields do not exist.

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Fig. 7 Fundamental properties.   Variation of magnetization with field for various temperatures, *left*, and variation of the saturation magnetization with temperature, *right* (courtesy of R. C. O'Handley).

Reading list

1. *Lectures on the Electrical Properties of Materials,* L. Solymar and D. Walsh, (Cambride Univ. Press, 199x) Sections 11.4 and 11.5, pages 306 - 314.

2. "Magnetic Materials", R. C. O'Handley, entry in *Encyclopedia of Physical Science and Technology*, Third Edition, ed. R.A. Myers (Academic Press, 2001).

3. *Diffraction from Materials*, Lyle H. Schwartz, Jerome B. Cohen, (springer Verlag, berlin, 1987), Section 1.5 "Naming Planes, Points, Directions", pages 11 - 15.

4. *Structure of Metals*, C. Barrett and T. B. Massalski,, (Pergamon Press, New York, 1980) Ch 11, pages 270-289
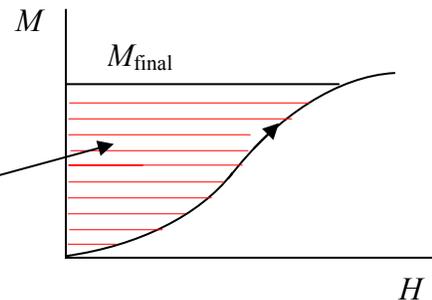
Useful concepts

Energy expended in magnetizing

For magnetic work as opposed to mechanical,
change variables: $F \rightarrow \sigma \rightarrow H$ (intensive)
$$dx \rightarrow \varepsilon \rightarrow dM \text{ (extensive)}$$

Magnetic variables:

Cgs: $B = H + 4\pi M$, $M = \chi H,\ dw = HdM$
MKS*:* $B = \mu_o(H + M),$ $M = \chi H,\ dw = \mu_o HdM$

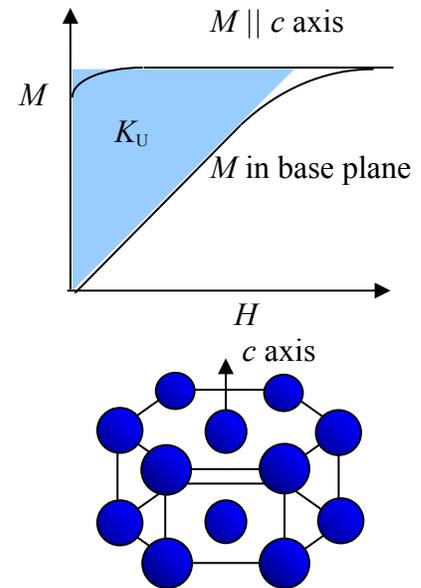$$\boxed{\frac{work}{vol} = \int_{0}^{M_{final}} HdM}$$ 8

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The area inside the hysteresis loop is the energy per unit volume of material that is lost per cycle. This lost energy is spent mostly moving domain walls over defects and also in irreversible rotation of **M**.

The energy required to magnetize a crystal can be different along different crystal directions if the crystal symmetry is low: This is called the magnetocrystalline anisotropy. In a uniaxial material (such as hexagonal Co) the energy associated with the **M** being saturated in different directions is given by:

$$g_{anis} = K_u \sin^2\theta.$$

The difference in energy for magnetizing along and orthogonal to the *c* axis is K_u. It is the shaded region between the to *M-H* curves. It is the energy expended in rotating the magnetization from its preferred direction along the *c* axis ($\theta = 0$) into a hard direction in the base plane.

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