

Lab week 3

Phase Transitions

Module γ -2: VSM study of Curie Temperatures¹

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- Objectives:**
- Understand magnetic and thermal effects associated with the *ferromagnetic/paramagnetic transition* at the Curie temperature.
 - Appreciate how a *first-order structural phase transformation* (in a ferromagnet) may affect magnetic properties and heat content.

Summary of tasks:

- Use vibration sample magnetometer (VSM) to measure the magnetization process, M vs. H , for Ni-Mn-Ga crystal below and above Curie temperature. Measure magnetization $M(T)$ in Ni-Mn-Ga crystal on increasing and decreasing temperature between 20 and 120°C at 500 Oe and 10 kOe.

Lessons to be learned: The Curie temperature defines a second-order magnetic transition between the low-temperature ferromagnetic state (long-range *ordering* of magnetic moments) and the high-temperature paramagnetic state (long-range *disorder* of magnetic moments). The other transition observed is a first-order structural transformation between the low-temperature, lower-crystal-symmetry martensite phase and high-temperature, higher-symmetry austenite phase. The latter transformation shows hysteresis because it is a first-order transformation; it is reflected in the magnetic susceptibility because of the change in magnetic anisotropy that occurs with the change in crystal symmetry.

- Use differential scanning calorimetry (DSC) to study the martensite transformation and Curie transition in Ni-Mn-Ga between 20 and 120°C. Calculate the heat of transformation in each case.

Lessons to be learned: Considerable heat is associated with the first-order transformation, less with the second-order transition. Distinguish endothermic and exothermic transitions.

¹ Acknowledgement: Lab Notes courtesy of Dr. Bob O’Handley with minor modifications.

Materials needed

Small Ni-Mn-Ga crystal, suitable for VSM measurements. The martensite transformation temperature, $T_m \approx 30 - 60^\circ\text{C}$, depends strongly on alloy composition; the Curie temperature, $T_C \approx 80 - 90^\circ\text{C}$, less so.

Equipment to be used

Vibrating sample magnetometer (VSM) and differential scanning magnetometer (DSC).

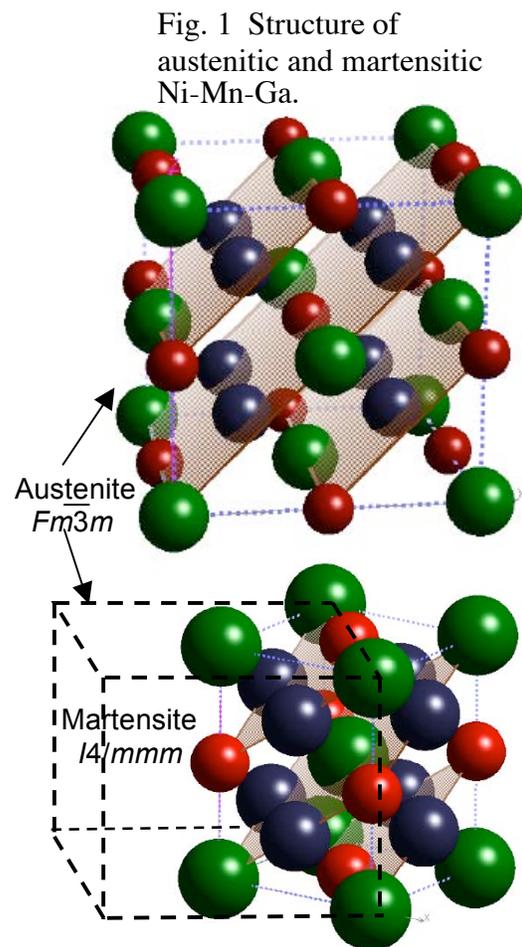
Background

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 $Fm\bar{3}m$ symmetry, as pictured in Fig. 1.

The composition you will study is close to the stoichiometric compound and is ferromagnetic with a Curie temperature of about 80°C . These compositions 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 60°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.

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 $I4/mmm$ symmetry (it is rotated 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 because the tetragonal distortion can occur along any of the three cubic $\langle 100 \rangle$ axes and the twin-boundary energy is small. 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.)

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:

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

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. 2.

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Fig. 2 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.

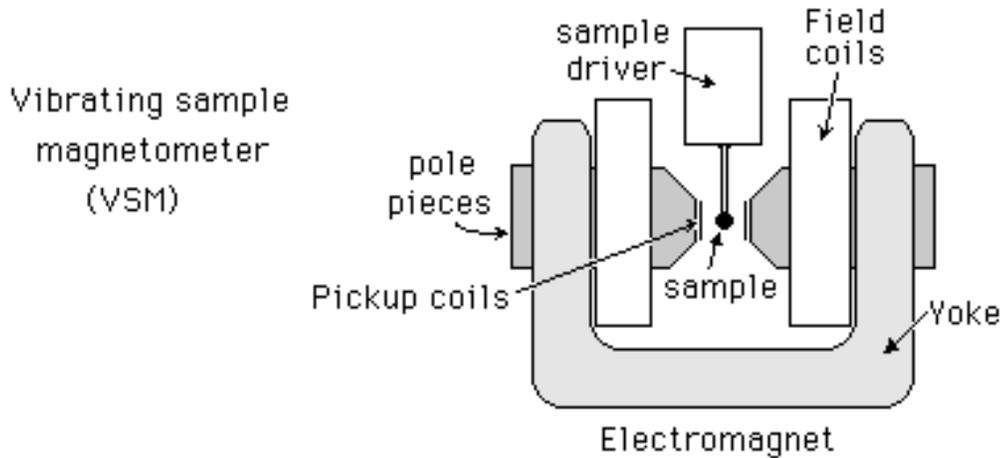
The *flux density* or magnetic induction inside a sample depends on the applied field and the sample magnetization, $B = \phi/A = \mu_0(H+M)$. Outside the sample ($M = 0$) the induction, $B = \mu_0H$, comes from the applied field and the H field due to the dipole moment of the sample. When the flux density 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. 3 and 4.

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Fig. 3. Direction of magnetic B field about a current-carrying solenoid is given by the right-hand rule.

We will use a vibrating sample magnetometer in which a sample is vibrated (± 1 mm at about 88 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. 4. 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.

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, $\mathbf{M} = N\boldsymbol{\mu}_m/V$ i.e. \mathbf{M} is the volume density of atomic magnetic moments, $\boldsymbol{\mu}_m$. The magnetization can be changed by application of a magnetic field, \mathbf{H} . Applying a field tends to line up the magnetization with the field. The sum of the magnetization and the \mathbf{H} field defines the flux density, \mathbf{B} : $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ (mks) or $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$ (cgs).

Quantity	Gaussian (cgs units)	S.I. Units (mks)	Conversion factor (cgs to S.I.)
Magnetic Induction (B)	G	T	10^{-4}
Applied Field (H)	Oe	Am^{-1}	$10^3 / 4\pi$
Magnetisation (M)	emu cm^{-3}	Am^{-1}	10^3
Magnetisation ($4\pi M$)	G	-	-
Magnetic Polarisation (J)	-	T	-
Specific Magnetisation (s)	emu g^{-1}	$\text{JT}^{-1}\text{kg}^{-1}$	1
Permeability (μ)	Dimensionless	H m^{-1}	$4\pi \cdot 10^{-7}$
Relative Permeability (μ_r)	-	Dimensionless	-
Susceptibility (χ)	$\text{emu cm}^{-3} \text{Oe}^{-1}$	Dimensionless	4π

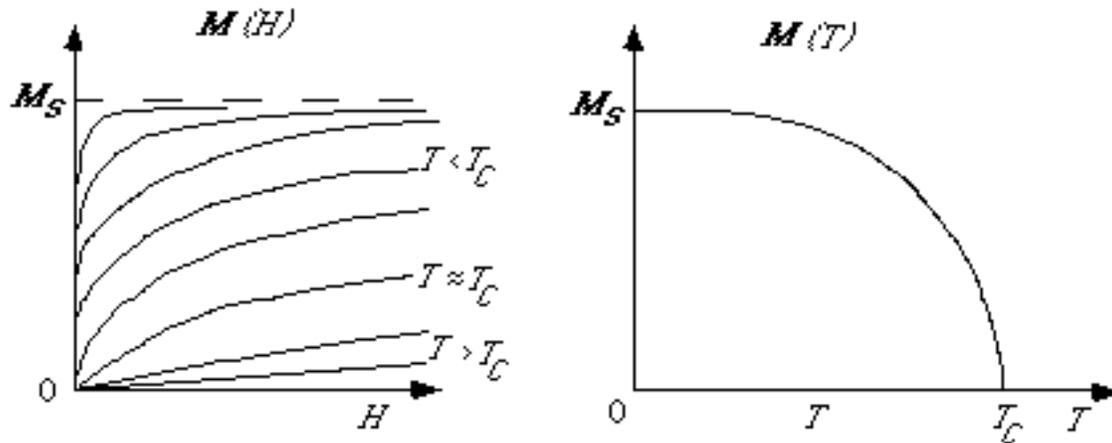
Table 1. Magnetic quantities in cgs and SI systems.

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. 5). 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.



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

Fig. 5 Fundamental properties. Variation of magnetization with field for various temperatures, *left*, and variation of the saturation magnetization with temperature, *right*.

Reading list

1. *Lectures on the Electrical Properties of Materials*, L. Solymar and D. Walsh, (Cambridge Univ. Press, 1988) 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).

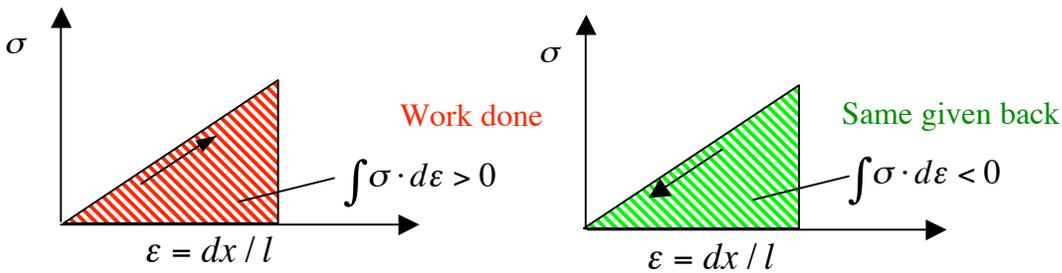
Useful concepts

Mechanical work, W :

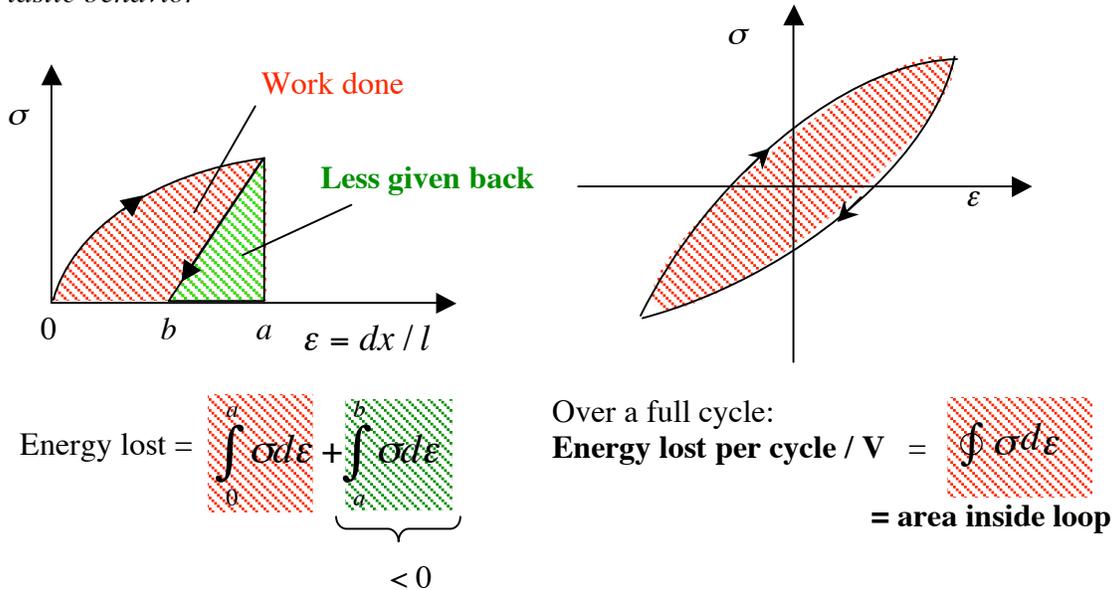
$$W = \int \mathbf{F} \cdot d\mathbf{x}$$

$$W/V = \int \sigma \cdot d\varepsilon$$

Elastic behavior



Plastic behavior



The convention in mechanical properties is to plot the *dependent* variable, strain, on the x axis. This was followed above. However, with magnetic properties, it is conventional to plot the magnetization or flux density (the dependent variable, the response to the applied field) as a function of the applied field. Keep this in mind when you compare the figures and integrals of mechanical and magnetic work.