Lecture 6: 09.21.05 Examples of work important in materials science and engineering

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Today:

Reading: M.W. Zemansky and R.H. Dittman, *Heat and Thermodynamics*, 7th Ed., Ch. 3 'Work,' pp. 49-68.

W.D. Callister, Jr., *Fundamentals of Materials Science and Engineering*, Ch. 18 'Magnetic properties,' pp. 730-744.

Supplementary Reading: -

Magnetic work[1]

- The work performed on magnetic materials by a magnetic field has similarities in form to the description of the effect of an electric field on polarizable materials (discussed in reading for today's lecture). One important difference is that electric dipoles always align with the direction of the electric field, while magnetic dipoles (magnetic moments) in materials may align parallel to an external magnetic field or anti-parallel to the magnetic field.

Types of magnetic materials

Ferromagnets

"PERMANENT MAGNETS"

- These are the materials you think of as magnets from everyday experience- the magnets on your refrigerator or the materials in the tip of a magnetic screwdriver. They maintain a magnetization in the absence of an externally applied magnetic field. Very few ferromagnetic materials exist; most ferromagnets contain iron, cobalt, or nickel. Ferromagnets tend to align their magnetic moments with an externally applied magnetic field.

FEW MATERIALS, PRIMARILY: Fe, Ni, Co

Non-ferromagnets

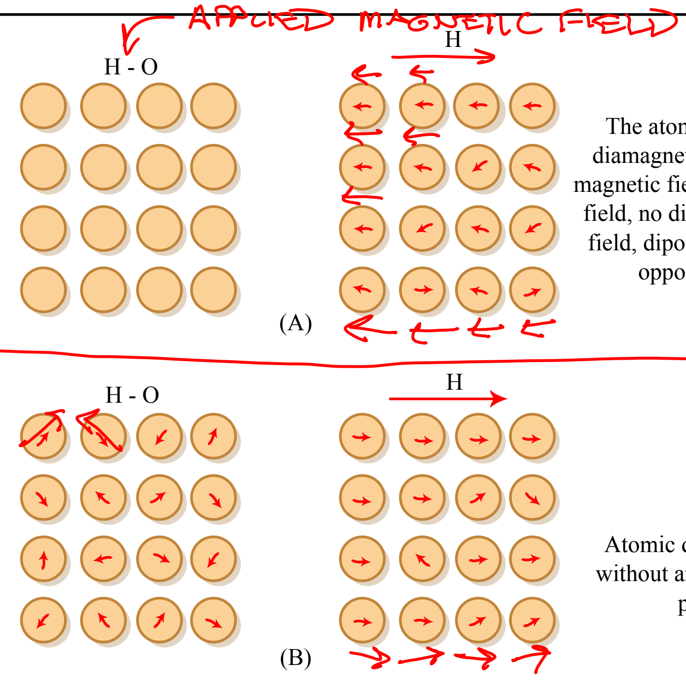
- Non-ferromagnets do not sustain their own magnetic field in the absence of an externally applied field. They are sub-classed into *paramagnetic* and *diagmagnetic* materials:

DIAMAGNETIC

- ANY MATERIAL, BUT THE EFFECT IS SO WEAK IT IS OF NO PRACTICAL UTILITY

PARAMAGNETIC

NO NET MAGNETIZATION IN ABSENCE OF $\vec{H}$, BUT ALIGN ON APPLICATION OF $\vec{H}$



(A)
The atomic dipole configuration for a diamagnetic material with and without a magnetic field. In the absence of an external field, no dipoles exist; in the presence of a field, dipoles are induced that are aligned opposite to the field direction.

(B)
Atomic dipole configuration with and without an external magnetic field for a paramagnetic material.

WORK IS DONE ON SYSTEM!

Figure by MIT OCW.

Work of magnetizing a paramagnetic material

- The work performed on a magnetic material by an externally applied magnetic field is given by:

$$\text{đ}w = \underbrace{V}_{\text{VOLUME}} \left(\underbrace{\vec{H}}_{\substack{\text{MAGNETIC}\\ \text{FIELD STRENGTH}}} \cdot \underbrace{d\vec{B}}_{\substack{\text{MAGNETIC INDUCTION}\\ \text{(RESPONSE PER UNIT VOLUME)}}} \right)$$

  - Where *V* is the volume of the system, *H* is the applied magnetic field, and *B* is the magnetic induction.
  - Analogous to the case of the electric displacement in polarizable materials, the magnetic induction *B* can be broken down as:

MAGNETIZATION OR MAGNETIC FIELD DENSITY

$$d\vec{B} = \underbrace{\mu_0 \vec{H}}_{\substack{\text{MAGNETIC}\\ \text{INDUCTION IN VACUUM}}} + \underbrace{\mu_0 \vec{M}}_{\text{MAG. INDUCTION IN MATERIAL}}$$

μ_o : *permeability of vacuum*: Relates the magnetization of empty space to the applied field
M : *induced magnetic field density* in the system

  - The induced magnetic field density can be modeled as a linear response to the applied magnetic field:

LINEAR ISOTROPIC MODEL: $\vec{M} = \underbrace{\chi}_{\text{SUSCEPTIBILITY}} \vec{H}$

$\chi \rightarrow$

  - The magnetic susceptibility χ measures the tendency of the material to respond to the applied field with formation of magnetic dipoles:

$\chi > 0$ PARAMAGNETIC

$\chi < 0$ DIAMAGNETIC (MAGNETIC DIPOLES ALIGN ANTIPARALLEL TO FIELD)

  - Expanding our definition for the magnetic induction above:

$$\vec{B} = \underbrace{\mu_0}_{\substack{\text{PERMEABILITY OF}\\ \text{VACUUM}}} \vec{H} + \mu_0 \vec{M} = \mu_0 \vec{H} + \mu_0 \chi \vec{H} = \underbrace{\mu_0 (1+\chi)}_{\mu} \vec{H}$$

$$\mu \equiv \mu_0 (1+\chi)$$

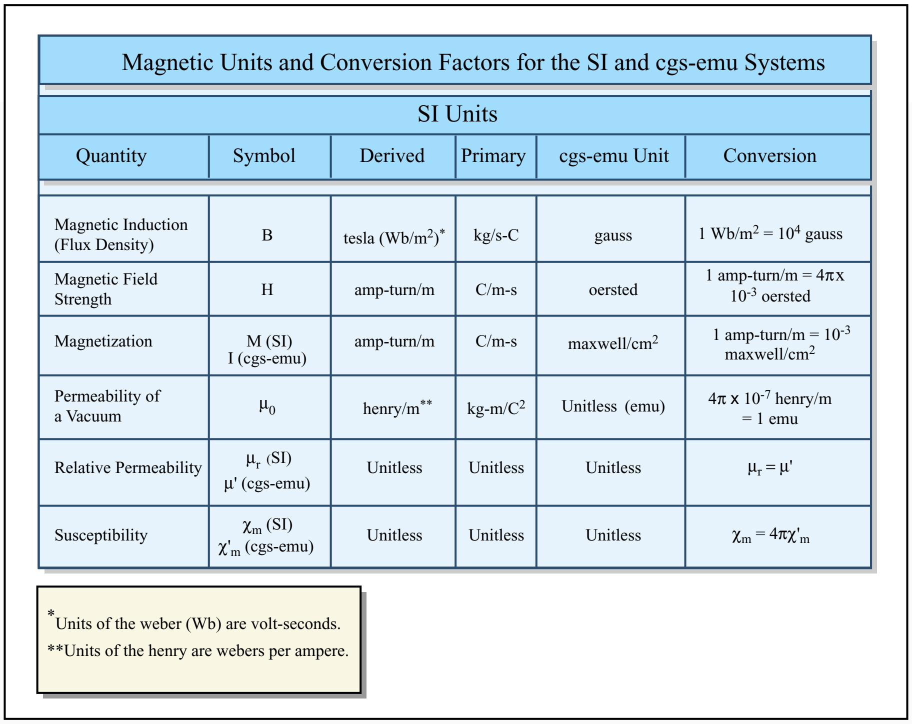
PERMEABILITY

- Where μ is the permeability of the material, analogous to the permittivity in polarization. Finally, the expression for the differential of work is:

$$dw = V(\vec{H} \cdot d\vec{B}) = V(\vec{H} \cdot (\mu d\vec{H})) = V\mu H dH$$

$$W = \int_0^{H_0} V\mu H dH = V\mu \frac{H_0^2}{2}$$

- …where the second equality arises for an isotropic material where the response is always exactly aligned with the direction of the externally applied magnetic field.



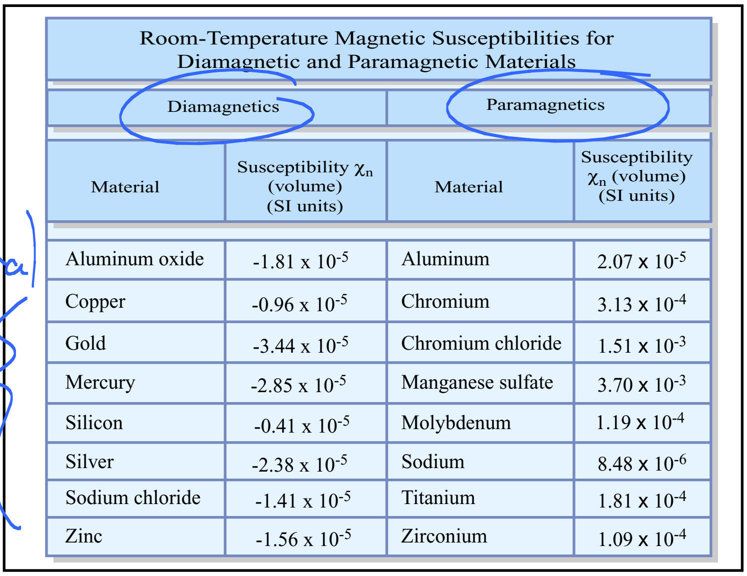
Magnetic Units and Conversion Factors for the SI and cgs-emu Systems					
		SI Units			
Quantity	Symbol	Derived	Primary	cgs-emu Unit	Conversion
Magnetic Induction (Flux Density)	B	tesla (Wb/m^2)*	kg/s-C	gauss	1 Wb/m^2 = 10^4 gauss
Magnetic Field Strength	H	amp-turn/m	C/m-s	oersted	1 amp-turn/m = 4π x 10^{-3} oersted
Magnetization	M (SI) I (cgs-emu)	amp-turn/m	C/m-s	maxwell/cm^2	1 amp-turn/m = 10^{-3} maxwell/cm^2
Permeability of a Vacuum	μ_0	henry/m**	kg-m/C^2	Unitless (emu)	4π x 10^{-7} henry/m = 1 emu
Relative Permeability	μ_r (SI) μ' (cgs-emu)	Unitless	Unitless	Unitless	$\mu_r = \mu'$
Susceptibility	χ_m (SI) χ'_m (cgs-emu)	Unitless	Unitless	Unitless	$\chi_m = 4\pi\chi'_m$

*Units of the weber (Wb) are volt-seconds.

**Units of the henry are webers per ampere.

Figure by MIT OCW.

Magnetic materials in materials science & engineering



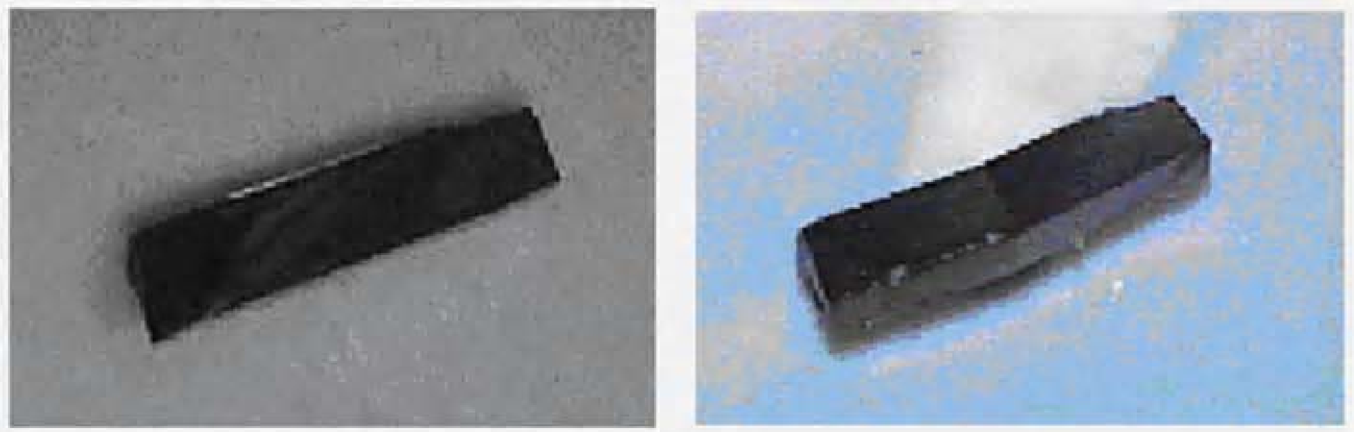
Room-Temperature Magnetic Susceptibilities for Diamagnetic and Paramagnetic Materials			
Diamagnetics		Paramagnetics	
Material	Susceptibility χ_n (volume) (SI units)	Material	Susceptibility χ_n (volume) (SI units)
Aluminum oxide	-1.81×10^{-5}	Aluminum	2.07×10^{-5}
Copper	-0.96×10^{-5}	Chromium	3.13×10^{-4}
Gold	-3.44×10^{-5}	Chromium chloride	1.51×10^{-3}
Mercury	-2.85×10^{-5}	Manganese sulfate	3.70×10^{-3}
Silicon	-0.41×10^{-5}	Molybdenum	1.19×10^{-4}
Silver	-2.38×10^{-5}	Sodium	8.48×10^{-6}
Sodium chloride	-1.41×10^{-5}	Titanium	1.81×10^{-4}
Zinc	-1.56×10^{-5}	Zirconium	1.09×10^{-4}

$$\chi_{diam} \simeq |0.1 - 0.01 \chi_{para}|$$

FERROMAGNETICS CAN HAVE $\chi \sim 10^6$ GREATER THAN PARAMAGNETIC MATERIALS

Figure by MIT OCW.

MAGNETIC WORK → MECHANICAL WORK



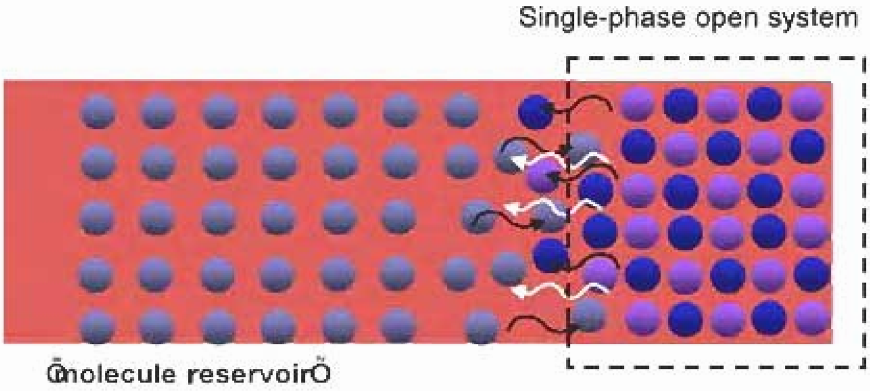
Ferromagnetic shape-memory alloys. Left, a 26 mm long crystal of Ni-Mn-Ga alloy at room temperature in zero field. Right, the same sample after application of a field of order 4 kOe by a permanent magnet. The metallic sample exhibits a kink at the twin boundary. (O'Handley research group[3])

Courtesy of Professor Robert O'Handley. Used with permission.

Chemical work

- Chemical work in materials can occur when the internal energy of a system changes in response to changes in the composition of a system. We have already mentioned the **chemical potential**, which is the driving force for chemical work.

Chemical work in single-phase materials



- What is chemical work and the chemical potential?
  - The chemical potential is a thermodynamic force [redacted] chemical [redacted]
    - In terms of 'F dx', a driving force multiplied by a displacement:

μ CHEMICAL POTENTIAL

SOURCES OF DRIVING FORCES: μ

① THERMAL MOTIONS THAT FAVOR RANDOM MIXING ← ENTROPY

② MOLECULAR INTERACTIONS THAT FAVOR OR DISFAVOR ← ENERGY
MIXING
↳ CHEMICAL REACTIONS

UNIQUE CHEMICAL POT. FOR EACH COMPONENT IN SYSTEM:

$$dw = \sum_{i=1}^{C} \mu_i dn_i$$

μ_i = CHEM. POT. OF i

dn_i = CHANGE IN MOLES OF i

C = # COMPONENTS

3 COMPONENTS A,B,C: $dw = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C$

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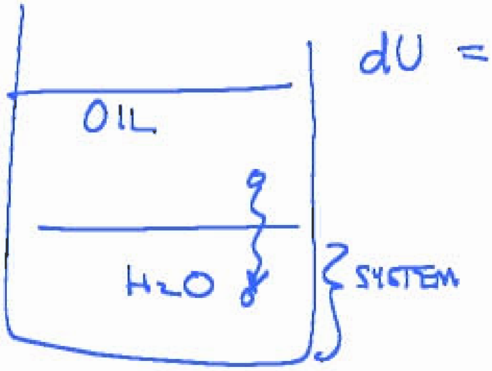
Example: chemical potential in phase-separated systems



SOLUBILITY CONTROLLED BY MAGNITUDE OF μ:

$$dU = \text{đ}q + \text{đ}w = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i$$

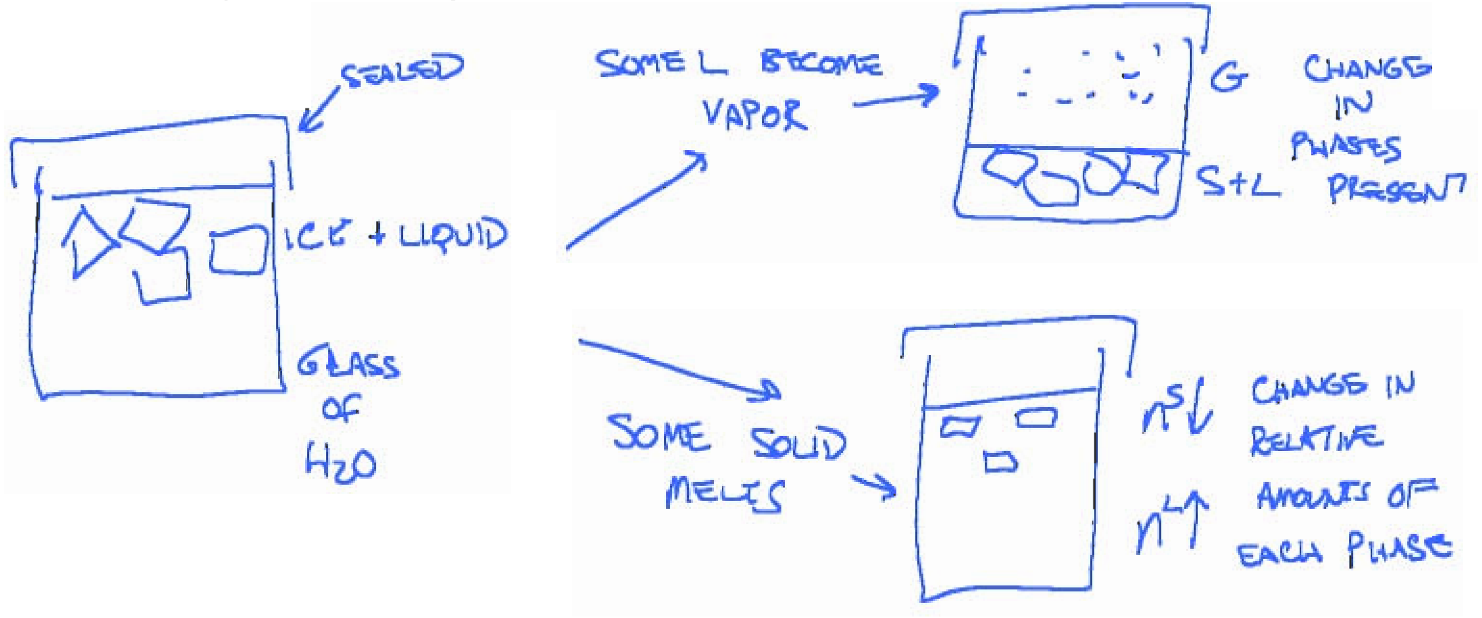
$$dU = \sum_{i=1}^{C} \mu_i dn_i$$

↳ IF $\mu_i > 0$ AND $dn_i > 0$ THEN $dU > 0$

" " AND $dn_i < 0$ THEN $dU < 0$

Chemical work and internal energy in multi-phase/multi-component systems

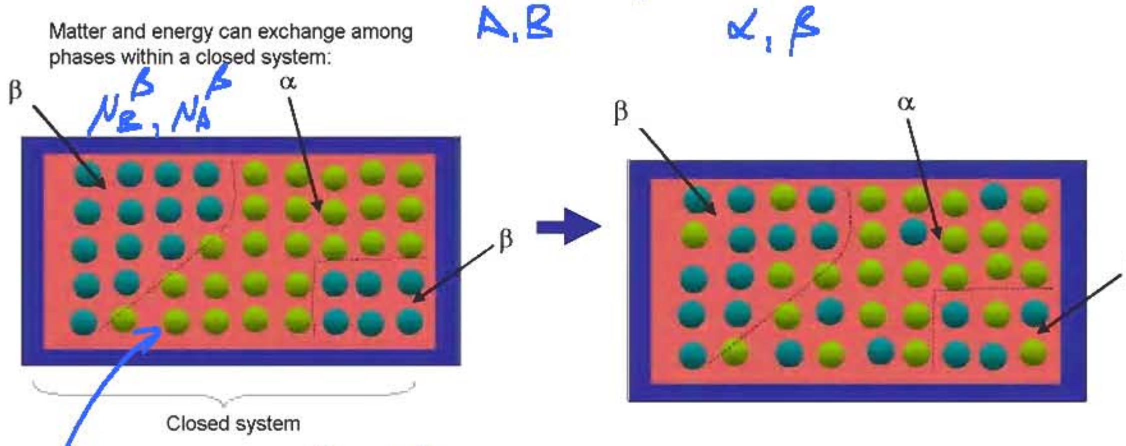
- Suppose now that we consider a closed multi-phase system, that cannot exchange molecules with its surroundings. Our glass of water with ice in it will work as an example, if we seal the top of the glass. Even though the system (ice + water) cannot exchange molecules with its surroundings, *chemical work can be performed by exchanging molecules between the phases present within the system, or creating new phases within the system.*



- When a multiphase system is also comprised of multiple components, which is an important case in materials science & engineering, then we can also have phases change their compositions by exchanging molecules:

2 COMPONENT, 2 PHASE
A, B α, β

n_B^β
n_A^β



$n_A^\alpha, n_A^\alpha, \mu_A^\alpha, \mu_B^\alpha$

Keeping track of the chemical potential in multi-component, multi-phase systems

- When a material is comprised of the most general case, containing C components and P phases, then the chemical work term contains contributions for each component in each phase. The general form for writing the reversible chemical work is:

$$dw = \sum_{i=1}^{C} \sum_{j=1}^{P} \mu_i^j dn_i^j = \mu_A^\alpha dn_A^\alpha + \mu_A^\beta dn_A^\beta + \mu_B^\alpha dn_B^\alpha + \mu_B^\beta dn_B^\beta$$

- …where we have separate sums over every component and every phase in the material. The sums account for the chemical energy parameters in each phase of a material. For example, if we consider the two-component, two-phase system shown schematically above, we have the following parameters:

	α phase:		β phase:
n_A^α	moles of A atoms in α phase	n_A^β	moles of A atoms in β phase
n_B^α	moles of B atoms in α phase	n_B^β	moles of B atoms in β phase
μ_A^α	chemical potential of A atoms in α phase	μ_A^β	chemical potential of A atoms in β phase
μ_B^α	chemical potential of A atoms in α phase	μ_B^β	chemical potential of A atoms in β phase

- In addition to moving molecules around, the chemical potential accounts for **chemical reactions**: changes of one species into another or the appearance of a new species due to chemical reaction. We will discuss this last important form of chemical work later in the term.

References

1. Carter, W. C. *3.00 Thermodynamics of Materials Lecture Notes* http://pruffle.mit.edu/3.00/ (2002).
2. Callister, W. D. *Fundamentals of Materials Science and Engineering* (John Wiley, New York, 2001) 524 pp.
3. O'Handley, R. http://web.mit.edu/bobohand/www/fsma.html#Ferromagnetic%20Shape%20Memory%20Alloys (2003).