Junior Honours Thermodynamics Assessed Problem 3: Magnetic Refrigeration.

Hand-in solutions to the physics teaching office by noon Tuesday, week 10.

Background : *This question examines the thermodynamics of magnetic refrigeration and the possibility of building a better domestic refrigerator than those based on gas-compression/expansion. It extends the simplified treatment given in the lectures.*

Magnetic refrigerators are commercially available for very low temperature applications below 1 K, but they are not used used at room temperature. Prototypes using Gadolinium as the magnetic material have been made and have achieved an efficiency of 60% of the ideal (Carnot) value. This can be compared to the highest efficiencies obtained with gas-compression/expansion of only 40%. The question examines the criteria for choosing better materials and the performance of one such material.

For a magnetic material the total work done on the material is $dw = -PdV + B.d\vec{\mathscr{M}}$ where we make the approximation that the induced magnetic field is small, and so $\vec{B}$ can be taken as $\mu_0\vec{H}$, and $\vec{\mathscr{M}}$ is the magnetic moment of the material [1]. It was also assumed that $\vec{\mathscr{M}}$ is parallel to $\vec{B}$ so that $\vec{\mathscr{M}}$ and $\vec{B}$ can be replaced by scalar quantities. The magnetisation (M) is also assumed to be homogenous with $\mathscr{M} = MV$. At given external conditions of temperature, applied field and pressure the most appropriate choice of thermodynamic potential is:

$$G = U - TS + PV - B\mathscr{M} \tag{1}$$

Having two types of work means that state variable can be expressed in terms of *three* other state variable, not just the two

$U =$ internal energy	$T =$ temperature
$S =$ entropy	$V =$ volume, $P =$ pressure
$\mathscr{M} =$ magnetic moment	$B =$applied magnetic field, assumed equal to $\mu_0 H$, the H-field is NOT enthalpy!)

required for gas processes. In this application the magnetic work is much greater than the PdV, so in principle we could omit the PV term entirely. However we choose to retain the suffix P in partial derivative, to remind ourselves that processes are at constant pressure.

(a) Show that the equilibrium entropy $S(T,B,P)$ is given by:

$$S(T,B,P) = -\left(\frac{\partial G}{\partial T}\right)_{B,P} \tag{2}$$

Derive similar expressions for $V(T,B,P)$ and $\mathscr{M}(T,B,P)$ in terms of partial derivatives of G.

(b) From the above expression for S show that the heat capacity at constant pressure and magnetic field $C_{P,B}(T)$ is related to the second derivative of G:

$$C_{P,B}(T) = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,B} \tag{3}$$

(c) Showing all the steps in your reasoning derive the following Maxwell relation

$$\left(\frac{\partial S}{\partial B}\right)_{P,T} = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{P,B} \tag{4}$$

This expression relates the isothermal isobaric change of entropy, as the magnetic field is changed, to the temperature dependence of the magnetisation at constant field and pressure. The second quantity is more straightforward to measure experimentally. The first quantity is what interests us for refrigeration applications.

(d) Derive the following expression for the small change in temperature, δT when the applied magnetic field is changed by δB reversibly and adiabatically at constant pressure.

$$\delta T = -\frac{T}{C_{P,B}(T)}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{P,B}\delta B \tag{5}$$

$C_{P,B}(T)$ and $\mathscr{M}(T,B,P)$ are materials properties measurable experimentally. The quantity $(\partial\mathscr{M}/\partial T)_{P,B}$ determines the magnetothermic*[2] property of the material. In a refrigerator the magnet would be repeatedly taken around a closed cycle in which it is magnetised in contact with a heat dump at room temperature and then demagnetised in contact with the compartment being cooled. What properties of gadolinium make it a promising material as the working substance of a domestic fridge*

The graph below shows the measured magnetisation [3] against temperature at atmospheric pressure for metallic Gd and for a candidate material for use in a room temperature magnetic refrigerator.

(e) Calculate the expected change of temperature of a thermally isolated piece of Gd when the field in which it is located is slowly reduced from an induction of 1.2 Tesla to 0.8 Tesla starting at a temperature of 300 K. (You may assume that the curve of M versus T does not change appreciably with B, for B in the range 0.8-1.2 Tesla and that the molar heat capacity of Gd is $C_p = 3R$ J/K/mole of atoms, independent of temperature and field. The formula mass of Gd is 157.25 grammes/mole.)

The value of $3R$ for the specific heat per mole of atoms is the value generally expected for lattice vibrations well above the Debye temperature - see later on in the condensed matter and statistical physics course modules

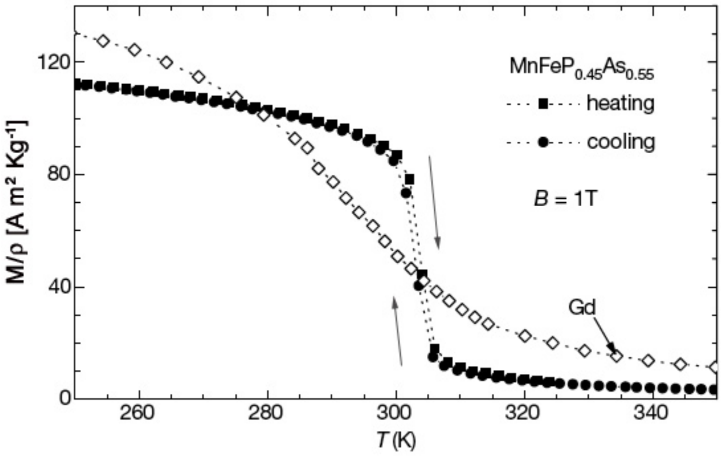

FIG. 1: The figure shows the measured magnetisation/density versus temperature in a field of 1 Tesla of $MnFeP_{0.45}As_{0.55}$ and Gd. From"Transition-metal-based magnetic refrigerants for room-temperature applications", O. Tegus et al. Nature **415** 150 (2002).

(f) The specific heat capacity is given by $C_{P,B} = (9/0.1659) \times R$ J/kg/K (The formula mass of $MnFeP_{0.45}As_{0.55}$ being 0.1659 kg per mole, and the magnetic contribution to $C_{P,B}$ is negligible) Explain the factor of 9, and give two observations based on Fig 1 that suggest that the change of magnetisation seen in $MnFeP_{0.45}As_{0.55}$ between 300 and 305 K corresponds to crossing a first order transition in this material.

(g) Derive the magnetic Clausius-Clapeyron-type relation between the change in entropy per volume $s = S/V$ and the change in magnetisation ΔM this transition.

$$\frac{\Delta S}{\Delta \mathscr{M}} = \frac{\Delta s}{\Delta M} = -\left(\frac{dB}{dT}\right)_p\Big|_{\text{transition}}$$

(h) Supposing further measurements show that the temperature *of the transition* increases with the applied magnetic induction at the rate 8 K/Tesla, estimate the change of temperature *of the sample* when sample is isentropically demagnetised by reducing the applied magnetic field from 1 T to 0 T starting from 300 K. [4]

(i) A NiMnInCo alloy has also been shown to have a large magnetocaloric effect [Nature Materials 11, 620626 (2012)]. Compare Fig 2 in that paper with Fig 1 here, and explain how the physics of the phase transition in this material contrasts with $MnFeP_{0.45}As_{0.55}$?

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[1] $\vec{B}$, the field inside the sample, is measured in Tesla. Script letters are used for extensive magnetic variables.
[2] A fancy long word meaning that magnetization changes with temperature
[3] Magnetisation, M, has SI units Am^{-1} and is an intensive quantity: it is the magnetic moment per unit volume. The figure shows M/ρ where ρ is the mass density, this is also an intensive quantity with units Am^2kg^{-1}
[4] Adiabatic means no heat leaves the system $\Delta Q = 0$, and here means that no net entropy $\Delta S = \Delta Q/T$ leaves the system. Entropy is transferred between magnetic and vibrational degrees of freedom.