Exam on "Fundamental Properties: Magnetism"

Lecturer: Graeme Blake

Friday January 27, 2017
5118.-152 and 5118.-156
9:00 – 10:30

Exam drafted by Graeme Blake, exam reviewed by Ron Tobey

Name:………………………………………………………………………………….

Student Number: …………………………………………………………………..

This exam paper contains 3 questions on 7 pages.

_____

For administrative purposes; do NOT fill the table

	Maximum points	Points scored
Question 1	11	
Question 2	8	
Question 3	11	
Homework	1.0	
Total	**42**	

The exam grade for the magnetism part is calculated as $1 + 9 \times$ (exam points/30)
The final grade for the magnetism part is $(0.9 \times$ exam grade$) +$ (homework grade).

Final grade: _____

Question 1 (11 points)

a. The figure below shows a plot of the inverse magnetic susceptibility of an unspecified material which at some low temperature shows magnetic ordering.

i. Is this compound ferromagnetic or antiferromagnetic? (1 point) Antiferromagnetic

ii. From the plot, estimate the approximate magnetic ordering temperature. (1 point) About 50 K

iii. Sketch on the plot how you expect the inverse magnetic susceptibility to evolve below 75 K. (1 point) See red curve below
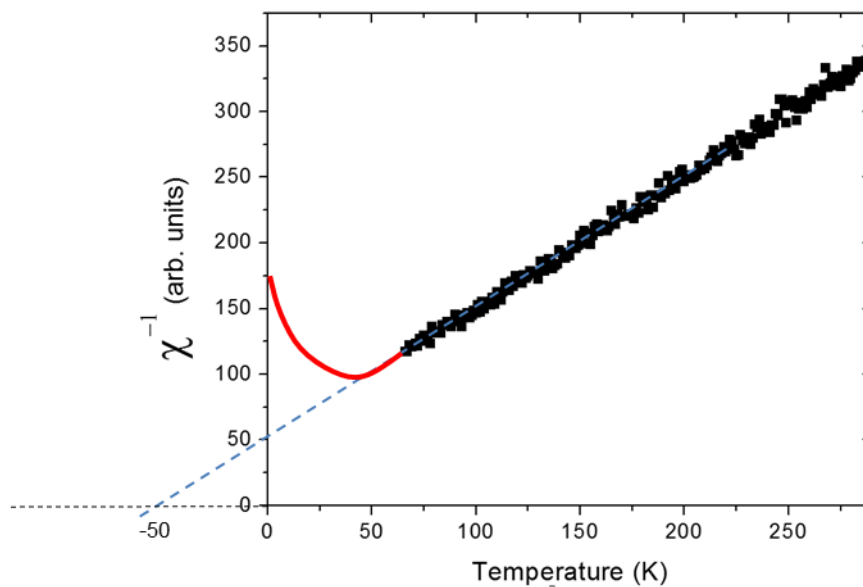

b. i. Sketch a plot of magnetization versus applied magnetic field (up to high fields) for the same material, assuming that the magnetic field is applied in the same direction as that of the spins. (1 point) Either of the plots below scores 1 point.
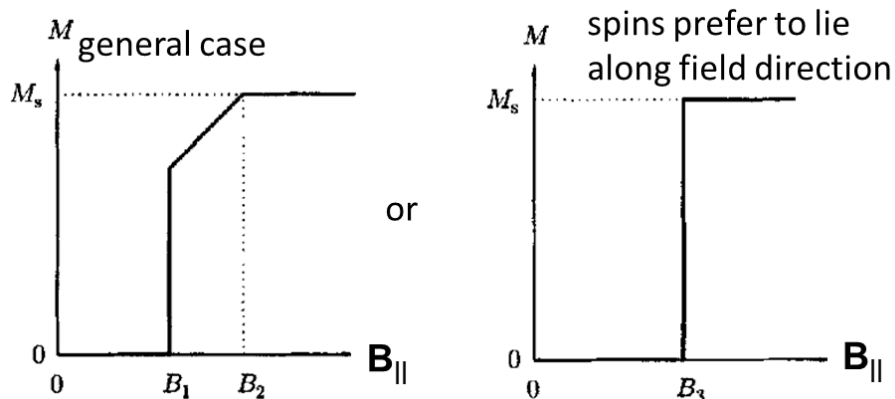
ii. Make a similar sketch for the situation where the field is applied perpendicular to the spins. (1 point)

The dependence will be something like the sketch below. The applied field will gradually rotate the spins and if one assumes that the rotation angle θ is proportional to $|\mathbf{B}|$, then M will follow roughly a $\sin\theta$ dependence, thus a $\sin B$ dependence. (This is an approximation, the spins might not smoothly rotate with increasing B).
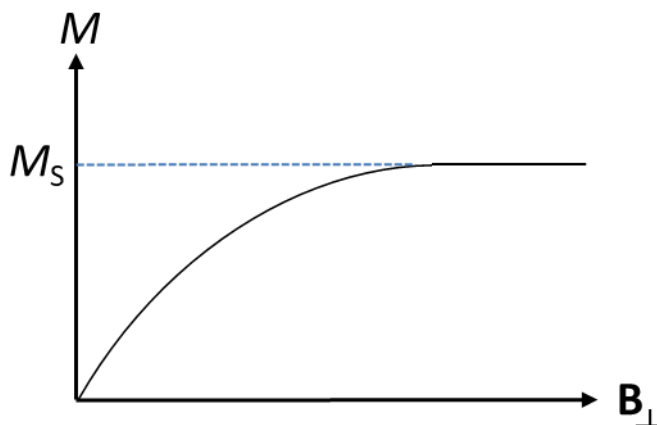

c. The compound $LaMnO_3$ shows a phase transition at 750 K in which the structure changes from cubic symmetry on the high temperature side, to an orthorhombic phase on the low temperature side in which the MnO_6 octahedra in the structure are distorted.

i. What kind of phase transition is this?
Explain, using an energy diagram for the d-levels of Mn^{3+} why this happens. (Note: here La has a formal charge of 3+ and Mn^{3+} has the electronic configuration $[Ar]3d^4$). (2 points)

The d-orbitals will split in energy like in the picture below.
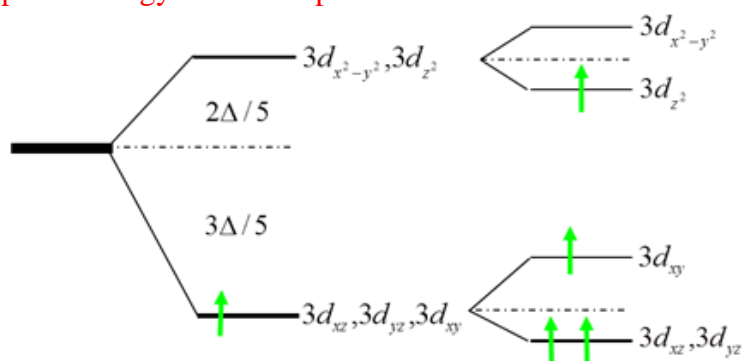
The system gains energy by the lowering of the dz^2 orbital. This results in a tetragonal distortion of the MnO_6 octahedron (1 point). At the phase transition temperature this Jahn-Teller distortion becomes ordered throughout the crystal and the symmetry is lowered from cubic to orthorhombic (1 point).

ii. Would you expect a similar transition in $CaMnO_3$? Why/Why not? (Note: here Ca has a formal charge of 2+). (1 point)

No, because Mn will have a formal charge of 4+. The d^3 state cannot gain energy via a Jahn-Teller distortion, so the structure will remain cubic.

iii. For the mixed-valence compound $La_{0.6}Ca_{0.4}MnO_3$, would you expect a ferromagnetic or an antiferromagnetic interaction between the moments on the Mn ions? Briefly explain the mechanism of this exchange interaction. Briefly explain whether you expect the compound to be a metal or an insulator. (3 points)

This compound contains mixed Mn^{3+} and Mn^{4+} cations. Therefore ferromagnetic double exchange will occur (1 point) by hopping of electrons from occupied to unoccupied e_g orbitals.
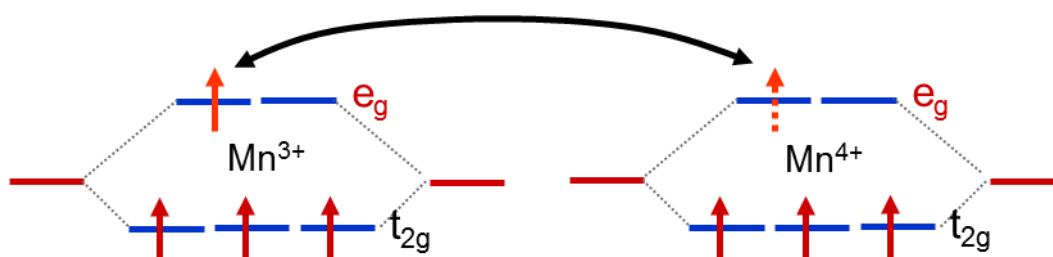

(Score 1 point for description or picture of mechanism)

The compound will be metallic because the hopping e_g electrons are mobile (1 point).

Question 2 (8 points)

The figure below shows a plot of the measured magnetic susceptibility versus temperature (in the form χT versus T) of a paramagnetic complex containing Fe^{3+} cations (electronic configuration $[Ar]3d^5$), each of which is coordinated by 6 ligands in octahedral geometry.
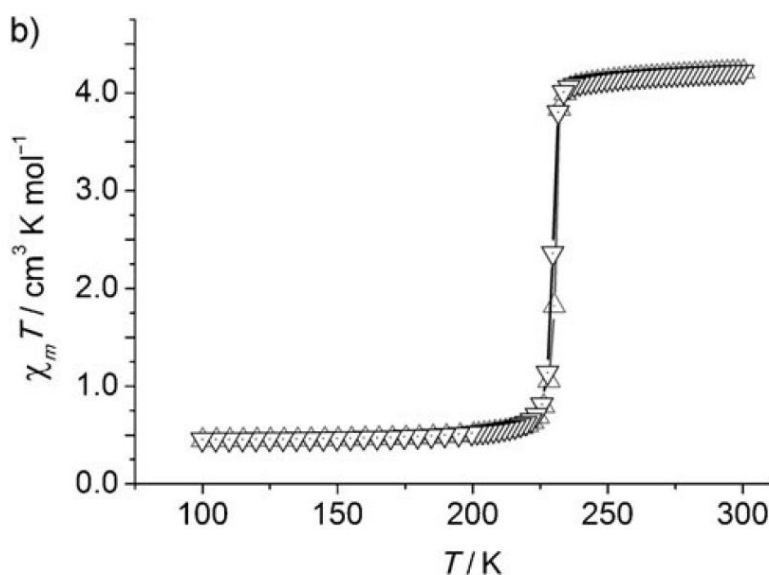
a. Using Hund's rules, predict the term symbol of the ground state of Fe^{3+}. (2 points)

1. Maximise S, hence S=5/2 (0.5 point)

2. Maximise L, hence L=0 (0.5 point)
3. Half-filled shell, thus L+S and L-S are the same: J=5/2 (0.5 point)
4. Term symbol is $^6S_{5/2}$ (0.5 point)

b. Give a possible explanation for the sudden change in magnetic susceptibility at 225 K. Is the measured magnetic susceptibility consistent with the predicted ground state of Fe^{3+}? Explain your answer. (2 points)

The change in susceptibility is a cross-over from the low-spin d^5 state (S=1/2) at low temperature to the high-spin d^5 (S=5/2) state at high temperature (1 point). The crystal field must be strong, larger than the electron pairing energy such that Hund's first rule is violated and the low-spin state becomes the ground state (1 point).

c. The effective magnetic moment of a magnetic ion is given by the formula $\mu_{eff} = g_J \mu_B \sqrt{J(J+1)}$

However, this predicted effective moment does not always agree well with experiment.

i. For Ni^{2+} (electronic configuration $[Ar]3d^8$) the predicted μ_{eff} is 5.59 μ_B whereas the measured μ_{eff} is 3.12 μ_B. Explain briefly why. (2 points)

For 1st row transition metals the orbital moment is usually quenched (1 point). The crystal field is often much stronger than the spin-orbit coupling. This means that J is replaced by S in the above equation and the expected μ_{eff} is $2\sqrt{2}$ μ_B, which is close to the measured value (1 point).

ii. For Eu^{3+} (electronic configuration $[Xe]4f^6$) the predicted μ_{eff} is 0 μ_B (zero) whereas the measured μ_{eff} is 3.4 μ_B. Explain briefly why. (2 points)

For the rare-earths the above equation usually holds because spin-orbit coupling is relatively strong. For f^6 Hund's rules predict that S=3 and L=3. For a less than half-filled shell J=L-S=0 (1 point). The effective moment is non-zero because low-lying excited states are populated (1 point).

Question 3 (11 points)

a. Explain why Fe, Co and Ni are ferromagnetic whereas all other metallic elements are not. (2 points)

For metals the Stoner criterium must be met for ferromagnetic ordering: $Ug(E_F) \geq 1$ where U is the Coulomb energy and $g(E_F)$ is the density of states at the Fermi level (1 point).
Fe, Co and Ni have especially high $g(E_F)$ and are the only elements in which the Stoner criterium are met, thus the only elements in which spontaneously spin-split bands are found (1 point).

b. Palladium (Pd) and platinum (Pt) are metals that are often said to be on the verge of ferromagnetism. Their paramagnetic susceptibility is greater than that predicted by the formula for Pauli paramagnetism, $\chi_P = \dfrac{3n\mu_0\mu_B^2}{2E_F}$ Explain why. (2 points)

For Pt and Pd the value of $Ug(E_F)$ is relatively high but still less than 1. Therefore these metals are Pauli paramagnetic (1 point). For such paramagnets the susceptibility is given by

$$\frac{\chi_P}{1-Ug(E_F)}$$

where the denominator is the so-called Stoner enhancement (1 point).

c. Why do ferromagnetic samples form magnetic domains in the absence of a magnetic field? Explain the difference between Néel walls and Bloch Walls. (2 points)

The formation of domains in the absence of an applied magnetic field costs energy (due to the formation of domain walls) but can minimize external demagnetising fields and thus lower the total energy of the system. At the edges of a sample small closure domains can be formed (1 point). In Bloch walls the spins rotate around an axis perpendicular to the wall; in Néel walls the rotation axis is parallel to the wall (1 point).

d. Ferromagnetic iron has a cubic crystal structure with lattice constant 2.856 Å. Its magnetic moment is 2.14 μ_B per atom, the exchange constant is equal to $k_B T_C$ where T_C = 1043 K, and the easy axis anisotropy is K = 4.8×10^4 J/m^3. Calculate the domain wall thickness (assume Bloch walls). (2 points)
(Note: k_B = 1.381 × 10^{-23} J/K)

The domain wall width is given by

$$\delta = \pi S \sqrt{\frac{2J}{Ka}}$$

where S is the total spin per atom, J is the exchange constant, K is the easy axis anisotropy and a is the lattice constant (1 point).

For Fe, $\mu \approx 2\sqrt{(S(S+1))} \mu_B = 2.14\ \mu_B$ therefore S = 0.68 (also accept values of S worked out using other methods such as $M = -g\mu_B m_s$).

Working this out, the width is $0.68\pi(1.44\times10^{-20}J / (4.8\times10^4\ J/m^3 \times 2.856\times10^{-10}\ m))^{1/2} = 70$ nm (1 point).

e. For iron the magnetic easy axis is the [100] direction. Sketch the magnetization as a function of applied magnetic field when the field is applied along the easy axis and when the field is applied along the [110] direction. (2 points)

Score 1 point for each curve on the plot below:
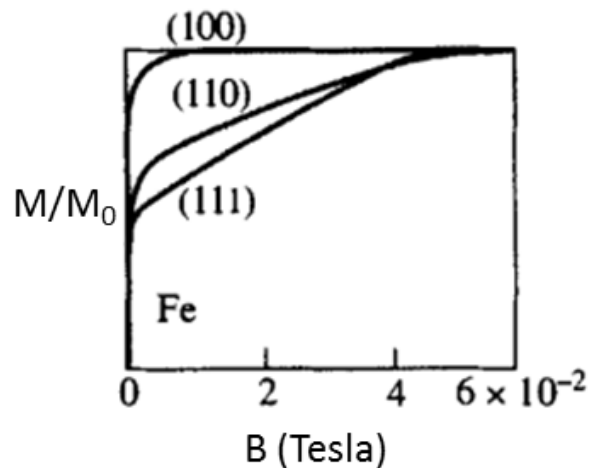
f. The interaction between the magnetic layers in an alternating non-magnetic metal/ferromagnetic metal multilayer structure can be either ferromagnetic or antiferromagnetic, depending on the thickness of the non-magnetic layers. Explain briefly in words why this is so. (1 point)

The interaction between the ferromagnetic layers occurs via the RKKY interaction. Both the sign and strength of the interaction depend on distance between interacting magnetic entities. Therefore the width of the non-magnetic layer can be tuned such that the interaction is ferromagnetic or antiferromagnetic.