

Exam on “Functional Properties: Magnetism”

Lecturer: Graeme Blake

Friday January 26, 2018
Martini Plaza
(half of the 09.00 – 12.00 time slot)

Exam drafted by Graeme Blake, exam reviewed by Caspar van der Wal

Name:.....

Student Number:

This exam paper contains 3 questions on 6 pages.
Please answer on the back of the page if you need more space.
A periodic table is supplied at the end of the paper (page 7).

For administrative purposes; do NOT fill the table

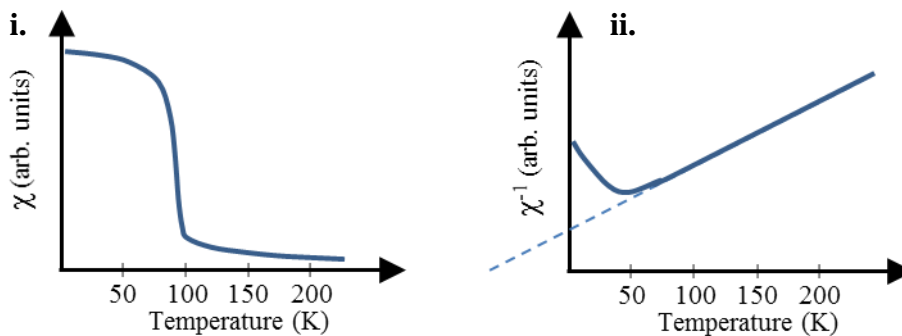
	Maximum points	Points scored
Question 1	10	
Question 2	14	
Question 3	11	
Homework	1 point of final score	
Total		

The exam grade for the magnetism part is calculated as $1 + 9 \times (\text{exam points}/35)$.
The final grade for the magnetism part is (exam grade) + (homework grade).

Final grade: _____

Question 1 (10 points)

- a. i. On the left-hand plot below, draw a typical magnetic susceptibility versus temperature curve for a *ferromagnet* with $T_C = 100$ K. (2 points)
- ii. On the right-hand plot below, draw a typical *inverse* magnetic susceptibility versus temperature curve for an *antiferromagnet* with $T_N = 50$ K. (2 points)



(also accept an answer showing χ diverging to infinity at T_C for the ferromagnet)

- b. Propose a suitable order parameter for a paramagnetic to antiferromagnetic phase transition and explain why this order parameter is suitable. (2 points)

A suitable order parameter would be the magnetization M (1 point). Although there is no net magnetization, M characterizes the magnetization of each sublattice, (1 point).

- c. Describe how the effective magnetic moment in the *paramagnetic* temperature region (above the ordering temperature of the ferromagnet or antiferromagnet) can be experimentally determined. (2 points)

Plot inverse susceptibility versus temperature. We can use the Curie law (1 point).

$$\chi \approx \frac{\mu_0 M}{B} = \frac{n \mu_0 \mu_{eff}^2}{3k_B T}$$

Then the effective moment can be obtained from the slope (Curie constant) of the line (1 point).

- d. LaBaNiO_4 , in which Ni^{3+} ($3d^7$) is octahedrally coordinated by oxygen, is a paramagnetic insulator. The effective magnetic moment of Ni is $\mu_{eff} = 1.75 \mu_B$ at 100 K but $\mu_{eff} = 3.90 \mu_B$ at room temperature. Give a possible explanation for these different values. (2 points)

The change in effective moment indicates a cross-over from the low-spin d^7 state ($S=1/2$) at low temperature to the high-spin d^7 ($S=3/2$) 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). (Other sensible suggestions can also score points)

Question 2 (14 points)

a. i. Using Hund's rules, determine the ground state of the Sm^{3+} cation (electronic configuration $4f^5$). (2 points)

1. Maximise S, hence $S=5/2$ (0.5 point)
2. Maximise L, hence $L=5$ (0.5 point)
3. Less than half-filled shell, thus $J = L-S$: $J=5/2$ (0.5 point)
4. Term symbol is ${}^6\text{H}_{5/2}$ (0.5 point)

ii. Calculate the effective magnetic moment of ground-state Sm^{3+} . (The Landé g-value for Sm^{3+} is $g_J = 2/7$.) (2 points)

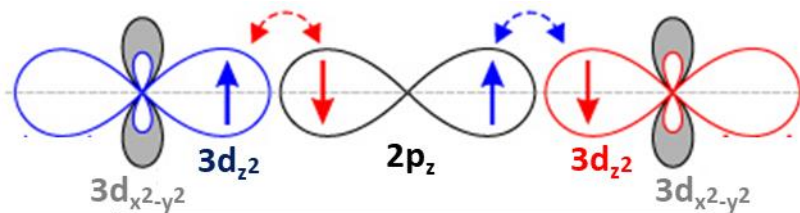
The effective magnetic moment of a magnetic ion is given by the formula $\mu_{\text{eff}} = g_J \mu_B \sqrt{J(J+1)}$ (1 point for formula)

Here this gives $\mu_{\text{eff}} = 0.85 \mu_B$. (1 point)

iii. The measured effective moment of Sm^{3+} is $\mu_{\text{eff}} = 1.74 \mu_B$. Does this agree with your calculated value? Comment on your answer. (2 points)

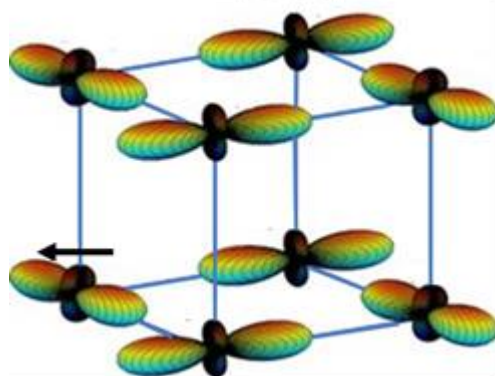
For the rare-earths the above equation for effective moment usually holds because spin-orbit coupling is relatively strong. (1 point) In this case the measured effective moment is much higher than the predicted value because low-lying excited states are populated (1 point). (Other sensible suggestions might score points)

c. Consider a metal oxide in which neighbouring transition metal atoms, both octahedrally coordinated by oxygen, each contain one unpaired electron in the $3d_{z^2}$ orbital. Superexchange can take place via the p_z orbital of a bridging oxygen atom in the geometry shown schematically below. Explain why superexchange in this geometry is antiferromagnetic. (2 points)

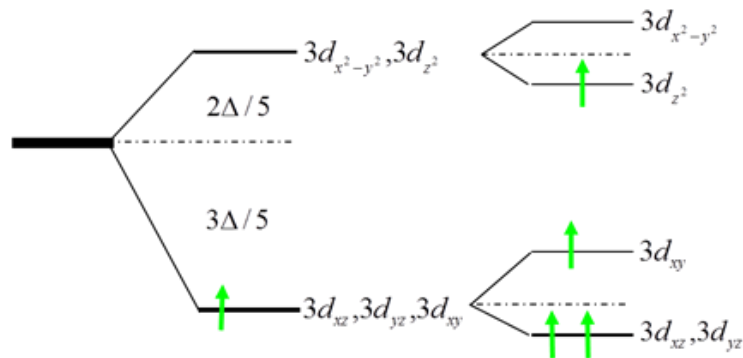


Here one has to consider whether electrons can be delocalized (lowering the kinetic energy) by mixing with excited states. In the antiferromagnetic case this is possible – the d_{z^2} orbital on one or both metals can be filled without breaking the Pauli exclusion principle (1 point). However, for ferromagnetic exchange excited states are forbidden because the Pauli exclusion principle would have to be broken (1 point).

d. LaMnO_3 possesses one unpaired electron in its manganese $3d_{z^2}$ orbital. These orbitals order spatially as shown in the picture below. Explain briefly why this happens. (Here Mn^{3+} has electron configuration $3d^4$ and manganese is octahedrally coordinated by oxygen.) (2 points)

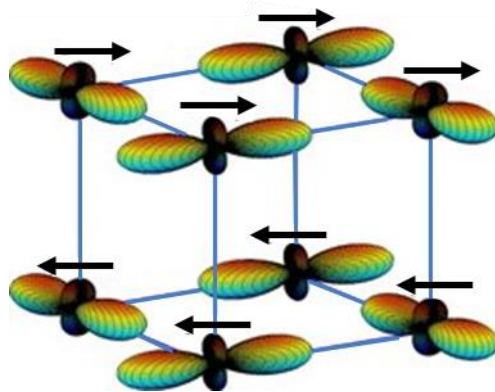


When in octahedral coordination, the d-orbitals of Mn^{3+} will split in energy like in the picture below. (1 point)



The system gains energy by the lowering of the d_{z^2} orbital. Due to electrostatic considerations, the d_{z^2} orbitals of neighbouring atoms will be orthogonal to each other to avoid electron repulsion as much as possible. (1 point).

e. The spin associated with one Mn^{3+} cation in LaMnO_3 is shown by the arrow (lower left on the diagram above). Indicate on the picture the directions of the other spins. Is the overall spin ordering in LaMnO_3 ferromagnetic or antiferromagnetic? (2 points)



(Parallel orbitals – antiferromagnetic interaction. Orthogonal orbitals – ferromagnetic interaction) (1 point).

Overall the ordering is antiferromagnetic (1 point).

f. LaMnO_3 is an insulator. When more than 20% of the trivalent La^{3+} in LaMnO_3 is replaced by divalent Sr^{2+} , the material becomes metallic. Suggest why. (2 points)

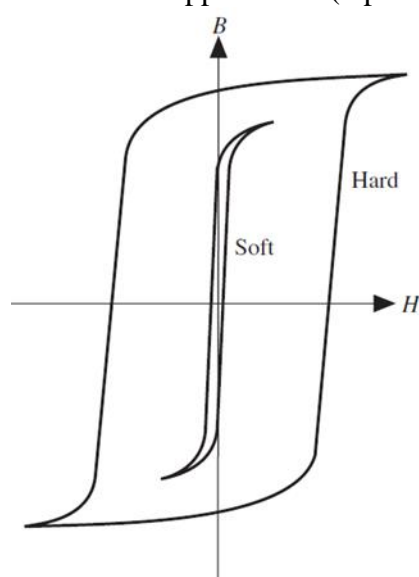
Manganese is now mixed valent (3+ and 4+). Mn^{3+} has one electron in the e_g orbitals, which are empty for Mn^{4+} (1 point). Then double exchange can occur by hopping between neighbouring e_g orbitals, leading to itinerant electrons and hence metallicity (1 point).

Question 3 (11 points)

a. When a ferromagnetic material is cooled down through its Curie temperature in the absence of an applied magnetic field, it forms ferromagnetic domains. Explain why these domains spontaneously form. (2 points)

The formation of domains in the absence of an applied magnetic field costs energy (due to the formation of domain walls) (1 point) 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).

b. Sketch a typical magnetization versus applied magnetic field loop for a soft ferromagnet and a hard ferromagnet. Give an example of an application for each type of ferromagnet and explain briefly why its properties are suitable for that application. (4 points)



(1 point for picture)

The area inside the loop corresponds to the energy dissipated as heat during one magnetization / demagnetization cycle (1 point).

Examples of applications for hard ferromagnets: permanent magnets, magnetic data storage – applications where a long-term magnetization is required and which is difficult to switch (1 point)

Examples of applications for soft ferromagnets: transformers – applications where the magnetization must be easy to switch and where as little energy as possible is lost in doing so (1 point).

c. Ferromagnetic nickel has a cubic crystal structure with lattice constant 3.524 \AA . There are 0.6 spins per atom in the ferromagnetic state, the exchange constant J is equal to $k_B T_C$ where $T_C =$

627 K, and the easy axis anisotropy is $K = -0.5 \times 10^4 \text{ J/m}^3$. Calculate the domain wall thickness (assume Bloch walls). (2 points)
 (Note: $k_B = 1.381 \times 10^{-23} \text{ J/K}$)

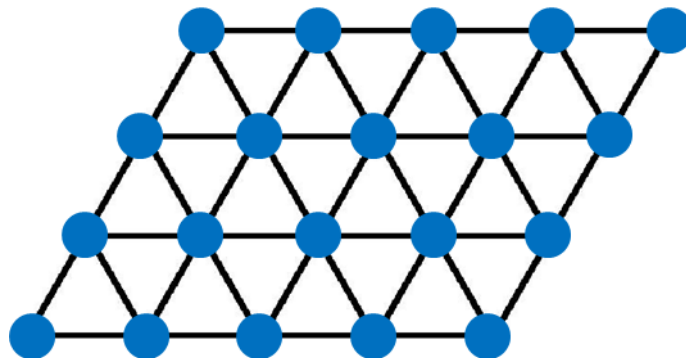
The domain wall width is given by

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

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).

Substituting values in the equation, the width is $0.6\pi(8.66 \times 10^{-21} \text{ J} / (0.5 \times 10^4 \text{ J/m}^3 \times 3.524 \times 10^{-10} \text{ m}))^{1/2} = 187 \text{ nm}$ (1 point).

d. YbMgGaO_4 is an insulator and has a crystal structure in which the magnetic Yb^{3+} cations ($S = \frac{1}{2}$) are arranged in two-dimensional layers with a triangular pattern as shown below by the blue circles. The sign of J for the exchange interaction between neighbouring Yb^{3+} cations is negative (antiferromagnetic). Discuss what the magnetic properties of YbMgGaO_4 might be and whether you would expect long-range magnetic ordering to occur in this compound. How could you test your prediction experimentally? (3 points)



Here the magnetic exchange interactions will be frustrated, because it is impossible to have an antiferromagnetic triangle (1 point). It might be possible to get long-range magnetic ordering, for example with spins pointing at 120 degrees to each around the triangle, but the ordering temperature will likely be greatly lowered (1 point). Experimentally, one could measure the magnetic susceptibility versus temperature and compare the observed ordering temperature with the frustration parameter obtained from a Curie-Weiss fit (1 point).

Other reasonable arguments can also score points here.