# Susceptibility of Paramagnetic sample by using Quinck's tube method

### 1. Aims

The aims of this experiment are to measure the magnetic susceptibility of a solution of manganese sulphate and to determine the magnetic dipole moment of a  $Mn^{2+}$  ion in units of the Bohr magneton,  $\mu_B$ .

## 2. Apparatus

- Electromagnet with rectifier current supply, Variac and ammeter 0-15A
- Hall probe
- U-tubes
- Digital micrometer with height gauge
- Magnifying viewer
- Manganese sulphate solution
- Manganese sulphate solution (3 x concentration)
- Distilled water
- Waste solution bottle
- Electronic balance
- Specific gravity bottle.
- Cotton buds, funnel, pipette, dropper.

## 3. Background

### (a) General

There are three main classes of experiment by which the susceptibility of a material may be measured. Quincke's method is based on the force experienced by a magnetised material in a non-uniform magnetic field and is a version of Gouy's method, which is specially adapted for liquids.

### (b) Quincke's Method

The **bulk** magnetic effects of materials are normally described in terms of the magnetisation M which may be defined as the magnetic dipole moment per unit volume. For a paramagnetic material the magnetisation M is induced by the applied field B and M is parallel to B.

The volume susceptibility is defined by the relations,

$$\mu_r = 1 + \chi, \qquad \chi = M / H \qquad (1)$$

where the magnetic intensity **H** is related to **B** through  $\mathbf{B} = \mu_0 \mu_r \mathbf{H}$ .

Since the relative permeability,  $\mu_r \approx 1$ , the magnetisation is given by,



Figure 1. Paramagnetic liquid in a uniform magnetic field

On an *atomic level*, the force  $F_{xm}$  in the vertical x-direction in Figure 1, on a magnetic dipole of moment *m* due to an applied magnetic field *B* is (omitting the vectors),

$$F_{xm} = m_x \frac{\partial B_x}{\partial x} + m_y \frac{\partial B_y}{\partial y} + m_z \frac{\partial B_z}{\partial z}$$
(3)

Thus using equations (2) and (3), the force <u>per unit volume</u> experienced at a point in the liquid in the U-tube illustrated in the figure is given by

$$F_{x-uvol} = \chi \frac{B_z}{\mu_0} \cdot \frac{\mathrm{d}B_z}{\mathrm{d}x}$$
(4)

providing B is in the horizontal *z*-direction throughout the volume occupied by the liquid. This equation can also be written

$$F_{x-uvol} = \frac{\chi}{2\mu_0} \cdot \frac{\mathrm{d}(B_z^2)}{\mathrm{d}x}$$
(5)

Equation (5) can also be derived by considering the stored energy, since the force is the negative of the gradient of the energy, which is proportional to  $B^2$  through the term  $\frac{1}{2}\vec{B}.\vec{H}$  per unit volume.

The force acting on an element of area A and length dx of the column of liquid is  $F_x A dx$  so the total force F on the liquid is,

$$F = A \int F_{xuvol} dx = \frac{A\chi}{2\mu_0} \int \frac{d(\mathbf{B}_z^2)}{dx} dx = \frac{A\chi(\mathbf{B}^2 - \mathbf{B}_0^2)}{2\mu_0}$$
(6)

where the integral is taken over the whole liquid. This means that B is equal to the field at the surface between the poles of the magnet and  $B_0$  is the field at the other surface, away from the magnet.

The liquid moves under the action of the total force F until it is balanced by the pressure exerted over the area A due to a height difference 2h between the liquid surfaces in the two arms of the U-tube. Allowing for the susceptibility  $\chi_a$  and density  $\rho_a$  of the air which the liquid displaces, it follows that,

$$\frac{A(\chi - \chi_{a}) \cdot (B^{2} - B_{0}^{2})}{2\mu_{0}} = 2Ah(\rho - \rho_{a})g, \qquad (7)$$

where g is the acceleration due to gravity, so that

$$(\chi - \chi_{a})(B^{2} - B_{0}^{2}) = 4\mu_{0}h(\rho - \rho_{a})g$$
 (8)

Thus equation 8 shows that by plotting h as a function of  $B^2$ , the susceptibility  $\chi$  can be determined directly from the slope of the graph.

In practice, *the corrections due to air are negligible*. There will also be a small but significant diamagnetic (i.e. *negative*) contribution to the susceptibility mainly due to the water. The total susceptibility of the solution is then given by  $\chi = \chi_{Mn} + \chi_{water}$ . This assumes that the number of water molecules per unit volume is not very different in the solution from that in pure water. In the present work you will correct  $\chi$  to yield the true value of  $\chi_{Mn}$  due to the presence of the manganous sulphate.

#### (c) The magnetic susceptibility $\chi$

Ions such as divalent manganese  $Mn_2^+$  possess a permanent magnetic dipole moment. A substance consisting of a system of such non-interacting magnetic dipoles behaves as a paramagnet. The dipoles tend to align parallel to a magnetic field giving a net magnetisation also parallel to the field. Thermal effects on the other hand tend to destroy this alignment, so the susceptibility of a paramagnet decreases as the temperature *T* is increased. It may be shown, using the methods of statistical mechanics, that at high temperatures ( $kT \gg mB$ ) the contribution  $\chi_{Mn}$  of the paramagnetic Mn ions to the volume susceptibility of the solution is given by,

$$\chi_{\rm Mn} = \frac{\mu_0 M}{B} = \frac{Nm^2 \mu_0}{3kT} = \frac{Np^2 \mu_B^2 \mu_0}{3kT}$$
(9)

where k is Boltzmann's constant and N is the number of Mn ions per unit volume and  $m = p\mu$ , where p is the magneton number defined in Appendix A. The 1/T dependence of  $\chi_{Mn}$  is known as Curie's Law.

The above theory assumes that the magnetic field acting on each ion is just the applied field B; field and contributions due to neighbouring magnetic ions are neglected. For dilute paramagnetic materials these other contributions are very small and the approximation is valid. This is not so for concentrated magnetic materials and ferromagnets and the effect of the neighbouring ions must be included.

#### 4. Experimental procedure

- **1.** Locate the flask of Manganese Sulphate solution. This flask is labelled with the mass of MnSO<sub>4</sub>.4H<sub>2</sub>O dissolved in a given volume of water.
- 2. Calculate the number of moles of  $Mn^{2+}$  ions per unit volume of the solution. 1 mole of a substance has a weight in grams equal to its molecular weight,  $W_m$ . The molecular weight is found by adding up the atomic weights of the constituent atoms of the molecule. If X grams of manganese sulphate,  $MnSO_4$  .4H<sub>2</sub>O were dissolved in  $V m^3$  of the solution, the number of moles is  $X/W_m$ . Each mole contains  $N_A$  (Avagadro's number) of molecules. Thus the number of molecules in  $V m^3$  is  $N_A X/W_m$  and N in equation 9 is  $N_A X/W_m V$ .
- 3. Measure the density  $\rho$  of your solution using a specific gravity bottle. The method here is to (a) weigh the bottle + stopper when it is dry and empty, (b) fill it with distilled water and weigh it again, (c) dry it with compressed air and fill it with your solution and weigh it again. The density  $\rho$  may be found, knowing the density of water  $\rho_{water}$ , from

$$\rho = \rho_{water} \frac{(c-a)}{(b-a)} \tag{10}$$

**4.** Calibrate the magnetic field against magnet current using the digital Hall probe. The magnet will run continuously with a current of 5A; for short periods at 10A and for very brief periods at 15A. Position the probe so that it gives positive values of B and use the stand provided so that it remains in the same position throughout your calibration.

If you record your calibration data with sufficiently small increments of current this will provide the best definition of the entire curve, which will be linear for small values of current and then the slope will decrease as magnetic saturation occurs in the material of the pole pieces. Note there may also be some magnetic hysteresis present and for a given current, the field may be slightly different, depending on whether the

current is increasing or decreasing. The magnetic saturation means that the highest values of current do not produce an equivalent increase in the values of the magnetic field. However you should measure the highest fields (subject to the current restrictions given above) since these will give the largest changes in the height of the magnetic liquids.

- **5.** Plot the calibration data of magnetic field versus current and try fitting the initial linear region with a straight line in Excel. Does the slope depend on whether you constrain the line to pass through the origin or not. The full calibration curve including the saturation region can be fitted with a second or third order polynomial.
- 6. Finally before the actual experiment, use the Hall probe to test if there is any variation of B across the region of the magnet pole pieces.

<u>Note:</u> The S.I. unit of B is the Tesla, although some of the older Hall probes may be calibrated in c.g.s. units such as Oersteds or Gauss. The conversion factors are:

$$1T = 10KOe = 10^4Oe = 10^4Gauss.$$

In the event of any problems consult a demonstrator.

WARNING: Scrupulous cleanliness of the U-tube is essential. Thoroughly clean the tube and rinse it well with distilled water before starting and dry it with compressed air. Make several sets of measurements to ensure consistency; false readings can arise from liquid running down the tube or sticking to the sides. Carefully swab down the inside of the U- tube with a cotton bud, to ensure that there are no droplets of liquid which might interfere with the plastic spacers on the rod which measures the height of the meniscus. Do not use the U-tube for longer than one laboratory period without recleaning. After cleaning ask the laboratory technician to dry the tube for you with compressed air.

- 7. Transfer some of your solution to the U-tube so that the meniscus is in the centre of the pole pieces. Take care to ensure that the surface of the liquid between the poles of the magnet is in the region where the field is greatest and reasonably uniform. Make sure that it is in the same starting position for all your experiments. The measuring rod should just touch the meniscus and if you wish you may set the micrometer scale to zero at this point.
- 8. Measure the displacement h of the column of liquid as a function of applied field B. Note that if you record your data now with the same small increments of current as your calibration data then you can access the B field values directly.
- 9. Dispose of all solutions when finished in the waste flask provided.
- **10.** There is a stronger (3 times) solution of manganese sulphate in a labelled bottle. Repeat the measurements with some of this stronger solution and use equation (9) to determine whether the data obtained are commensurate with this new concentration.
- 11. Determine the susceptibility  $\chi$  using equation (8). Compare  $\chi$  with the value given in Kaye and Laby, which you should note is the mass susceptibility of the parent crystalline material (units m<sup>3</sup> kg<sup>-1</sup> at 20 °C). You can easily change this to a volume

susceptibility by multiplying by the density of the salt ( $\rho_{MnSO4.4H20}=2.95 \times 10^3$  kg m<sup>-3</sup>). The value you obtain will be different from the susceptibility of your solution since the number density of ions in the salt is larger than the number density of ions in your solution by a factor of about 10.

- 12. Make estimates of  $\chi_a$ ,  $\rho_a$  and  $B_0$  in equation 8 and show that their effects are negligible.
- **13.** From your measured susceptibility  $\chi$  obtain  $\chi_{Mn}$  by correcting for  $\chi_{water}$  (remember water is diamagnetic). [Diamagnetic volume susceptibility of water  $\chi_{water} = -0.90 \times 10^{-5}$ ]
- **14.** Use equation (11):

$$\chi_{\rm Mn} = \frac{Np^2 \mu_B^2 \mu_0}{3kT}$$
(11)

and your value of N to determine the effective number p of Bohr magnetons of a  $Mn_2^+$  ion and compare your value with those given in Appendix A.

### **Appendix A: Magnetic moment values**

The magnetic susceptibility of a substance is related to the magnetic dipole moments of its individual atoms or ions. The total angular momentum of an atom or ion arises from both the orbital motion and the spin of the electrons. The magnetic dipole moment can be expressed in the form

$$m = p \mu_{B}$$

where p, the magneton number, is the dipole moment in units of the quantity  $\mu_B$ , which is known as the Bohr magneton. The Bohr magneton is the atomic unit of magnetic moment defined by,

$$\mu_B = eh/4\pi m_e$$

where, in this equation, e and  $m_e$  are the electronic charge and mass and h is Planck's constant. The dimensionless magneton number p is usually between 1 and 10 for atomic systems.

The rules for calculating *p* can be summarised as follows,

- (i) the unfilled electron shells for any atom or ion can be found in standard tables.
- (ii) the quantum numbers of the individual electrons can be added

$$L = \sum_{i} l_i$$
 and  $S = \sum_{i} s_i$ ,

to give the largest values of L and S consistent with the Pauli Exclusion Principle

(iii) the total quantum number J can be found from

J = L - S first half of the electron shell

J = L + S second half of the electron shell

(iv) the magneton number p is given by,

$$p = g\sqrt{J(J+1)}$$

where g the so called Landé splitting factor

$$g = \left\{\frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}\right\}$$

takes into account that the spin effectively creates twice as much magnetic moment as the orbital motion.

(v) the results of these calculations are tabulated in most textbooks on condensed matter physics, see the two Tables 1 and 2.

No of electrons in 3d shell	Ion	S	L	J	р
0	Ca <sup>2+</sup>	0	0	0	0
1	$\mathrm{Sc}^{2+}$	1/2	2	3/2	1.55
2	Ti <sup>2+</sup>	1	3	2	1.63
3	$V^{2+}$	3/2	3	3/2	0.77
4	$Cr^{2+}$	2	2	0	0
5	$Mn^{2+}$	5/2	0	5/2	5.92
6	Fe <sup>2+</sup>	2	2	4	6.71
7	$\mathrm{Co}^{2+}$	3/2	3	9/2	6.63
8	Ni <sup>2+</sup>	1	3	4	5.59
9	Cu <sup>2+</sup>	1⁄2	2	5/2	3.55
10	$Zn^{2+}$	0	0	0	0

Table 1 Magneton numbers p for some transition metals (TM<sup>2+</sup> free ions)

No of electrons in 4f shell	Ion	S	L	J	g	р
0	La <sup>3+</sup>	0	0	0		0
1	Ce <sup>3+</sup>	1/2	3	5/2	6/7	2.54
2	$Pr^{3+}$	1	5	4	4/5	3.58
3	$Nd^{3+}$	3/2	6	9/2	8/11	3.62
4	$Pm^{3+}$	2	6	4	3/5	2.68
5	$\mathrm{Sm}^{3+}$	5/2	5	5/2	2/7	0.84
6	Eu <sup>3+</sup>	3	3	0		0
7	$\mathrm{Gd}^{3+}$	7/2	0	7/2	2	7.94
8	$\mathrm{Tb}^{3+}$	3	3	6	3/2	9.72
9	Dy <sup>3+</sup>	5/2	5	15/2	4/3	10.63
10	Ho <sup>3+</sup>	2	6	8	5/4	10.58
11	Er <sup>3+</sup>	3/2	6	15/2	6/5	9.59
12	$\mathrm{Tm}^{3+}$	1	5	6	7/6	7.55
13	Yb <sup>3+</sup>	1/2	3	7/2	8/7	4.54
14	Lu <sup>3+</sup>	0	0	0		0

Table 2 Magneton numbers p for rare earths ( $RE^{3+}$  free ions)