CHAPTER 3

EXPERIMENTAL
3-1 PRELIMINARIES

Magnetic measurements with single crystals are very important. The measurement of average susceptibility on powder samples comes a rather poor second best to the determination of susceptibility tensor of a single crystal; it fails to give information about the anisotropy of the crystal which is a sensitive index for the crystal field. The single crystal measurements yield more information which help us get a deeper insight into the nature of interactions of the paramagnetic ion with its surroundings. Determination of magnetic properties involve measurement of magnetic anisotropy and the principal susceptibilities. For the uniaxial crystal one has to determine the magnetic anisotropy $\Delta \chi = \chi || - \chi _{\perp}$ and the principal magnetic susceptibility perpendicular to the symmetry axis ($\chi _{\perp}$) or the principal magnetic susceptibility parallel to the symmetry axis ($\chi ||$), or both in cases where $\chi || > \chi _{\perp}$. The experimental setup for magnetic measurements on single crystals both at room and low temperatures is described in the following sections.

3-2 MAGNETIC MEASUREMENTS

3-2.1 Measurements of Magnetic susceptibility

Faraday technique is employed to measure the absolute magnetic susceptibility. In this method, the crystal is placed in an inhomogeneous horizontal magnetic field with a constant field-gradient $[H_z \cdot (dH_z/dx) = \text{constant}]$ in the vertical direction. The force acting on the crystal is measured by a sensitive taut band electromagnetic balance.
fabricated in the laboratory. The balance (P 3.1) works on the electrodynamic method of balancing the magnetic force acting on the crystal. A small rectangular coil of thin copper wire is placed in the radial field of a permanent magnet fitted with an iron core; the coil is held in place with a taut band suspension made of platinum [or phosphorbronze] ribbon to enable it to move freely about the suspension. A pyrex glass beam fitted with a mirror is attached rigidly to the coil. From one end of the beam the crystal is suspended by a thin quartz fibre through the hang-down tube in the pole gap of the electromagnet. The balance is enclosed in a rectangular glass box or a bell jar. The balance is continuously nulled by a microprocessor based programmable current control module. A pair of specially designed Faraday pole caps [1] is used to produce a constant field gradient. A microprocessor controlled digital power supply unit delivers power to the electromagnet. The force acting on the crystal is \( F = (K - K_a) V H_z (dH_z/dx) \) where \( V \) is the volume of the crystal and \( K \) is the volume susceptibility of the crystal and \( K_a \), that of the medium. The torque produced by this force is automatically counterbalanced by passing a current through the balance coil employing the balance current control module; the current reading \( I \) is noted. The torque acting on the balance coil (BC) about the suspension is \( (N A H I)/(10 \times 980) \) gm cm, where \( N \) is the number of turns, \( A \), the effective cross-sectional area of the coil and \( H \), the strength of the magnetic field (in Gauss) of the local magnet, and \( I \) is the current through the coil in Amperes. Hence the force acting on the crystal is proportional to the current \( I \).

If \( I_s \) and \( I \) are the balancing currents for the standard specimen and the crystal, and \( F_s \) and \( F \) are the corresponding forces, then

\[
F_s = C (m_s/\rho_s)(K_s - K_a) \propto I_s
\]
P 3.1  Taut band balance
\[ F = C \left( \frac{m}{\rho} \right) (K - K_0) \propto 1 \]

where \( C \) is the constant of proportionality.

Hence, \( \frac{(l_x/l)}{(m_s/m)} \left[ \left( \chi_m - (K_{m/\rho}) \right) / \left( \chi_{m/s} - (K_{m/\rho}) \right) \right] \right) \), \( (K/\rho) = \chi \)

or, \( \chi_m = \frac{1}{l_s} \frac{(m_s/m)}{\left[ \chi_{m/s} - (K_{m/\rho}) \right]} K_{m/\rho} \)

where \( \chi_m \) is the mass susceptibility of the sample and \( K, m, \rho \) are the volume susceptibility, mass, and density of the crystal; the subscript \( s \) refers to standard specimen.

Thus in terms of the susceptibility of the standard specimen the susceptibility of the crystal can be determined. Manganese ammonium sulfate hexahydrate (\( \text{Mn(NH}_4\text{)}_2\text{(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \)) single crystals were grown and grinding them into powder, is used as standard sample.

The programmable digital power supply (for electromagnet) and the balance are interfaced with a PC making the measuring process fully automatic; the data are stored directly in the hard disk.

3-2.2 Measurement of Magnetic Anisotropy

The magnetic anisotropy of a single crystal in a plane is measured by a quartz torque balance. The schematic diagram of the set up is shown in Fig. 31. The crystal under study is attached to a long straight rod (6) of uniform cross section with the help of another short and comparatively thin pyrex rod (7). A calibrated uniform fine quartz fibre (4) (of suitable torsional constant for the crystal under study) is attached to the pyrex rod (6). The other end of the quartz fibre is fixed to a brass pin (3) which is inserted into the
Fig. 3.1
central bore of a torsion head (2) with a vernier which moves over a circular graduated scale. The torsion head is coupled to an ac motor (1) for smooth rotation of the pin in either direction i.e. clockwise or anticlockwise. A small mirror (5) is attached to the long pyrex rod (6) and a light spot reflected by it indicates the angular movement of the rod and hence that of the crystal. The alignment of the maximum susceptibility direction of the crystal in the horizontal plane with the magnetic field direction is achieved by rotating the magnet. The zero position of the suspension system and that of the magnet is obtained when no deflection of the light spot is observed on switching on the magnetic field (~ 5 KG). The magnet is rotated from the zero position through an angle less than 45 degree and preferably greater than 30 degree. When the magnetic field is switched on, the crystal will experience a couple to bring the maximum susceptibility direction along the magnetic field. The crystal is restored to its initial position by rotating the torsion head slowly with the help of a motor, and the reading of the torsion head on the circular scale is noted. For better accuracy, these readings of the torsion head are taken by rotating the magnet in both clock and anti-clock directions.

The molar magnetic anisotropy is then obtained using the equation

$$\Delta \chi = \left[ \frac{\pi c M \alpha}{90 H^2 m \sin 2\theta} \right] \text{ c.g.s. e.m.u.}$$

Where c is the torsional constant per unit twist, M, the molecular weight, m, the mass of the crystal, \( \theta \), the angle through which the magnet is rotated, \( \alpha \), rotation of the torsion head and \( H \) is the magnetic field. The correction for the magnetic anisotropy of the suspension system was made appropriately.
The torsional constant, $c$, of the quartz fibre is determined by suspending a glass disc of known moment of inertia ($I$) in an air tight glass tube, and observing the time period, $T$, of the torsional oscillations using the relation

$$c = 4 \pi^2 \left( \frac{1}{T^2} \right),$$

where $T_0 \approx T \left[ 1 - \left( \frac{\lambda}{2\pi^2} \right) \right]$, $\lambda$ being the logarithmic decrement due to air damping. The air damping can be neglected without any loss of accuracy if a small disc with a small time periods is used for measuring ‘$c$’. The magnetic field is calibrated using a CuSO$_4 \cdot$ 5H$_2$O crystal as the standard sample. The value of $\Delta \chi$ with $c$- axis vertical is used [2,3] in the calculation of $H$.

### 3.3 LOW TEMPERATURE SETUP

#### 3.3.1 Absolute susceptibility

The absolute magnetic susceptibility of a single crystal is measured in the temperature range, 300 - 13K; the low temperature environment was generated by an APD closed cycle helium refrigerator. In the following subsections we discuss the low temperature arrangements.

#### 3.3.1a Closed cycle refrigerator

The closed cycle helium refrigerator is formed from basic the modules which include a water cooled helium compressor, an expansion engine, interconnecting hoses, and interfaces; the modules are shown separately in Fig.3.2. The expander module is the
Fig. 3.2
Fig. 3.3
P 3.2 Computerized susceptibility measurement Lab.
refrigerator, the compressor module supplies refrigerant (here helium gas) to the expander, and the interconnecting hoses carry refrigerant between the compressor and the expander module. Together, they form a basic closed loop system. The expander module is fitted to the Faraday attachment where the two cold stations of the expander are thermally strapped to the hang-down tube, the lower end of which forms the crystal chamber. The upper end of the hang down tube is connected to the base-plate of the balance through a rubber vacuum hose and the complete arrangement is shown in Fig 3.3. The crystal chamber and the space within the vacuum shroud are independently connected to the vacuum system. The hang-down tube in which the crystal is suspended with a quartz fibre is evacuated along with the balance chamber and flushed twice with pure helium. Finally, helium is introduced and the pressure inside the tube is maintained at an optimum level to allow for good heat conduction between the crystal and the chamber wall and to avoid any oscillation of the balance due to strong convection currents. This arrangement led to stabilization of the crystal temperature in about twelve minutes. High vacuum ($\sim 10^{-4}$ torr) was maintained in the space between the vacuum shroud and the hang-down tube, the later being wrapped around with aluminized mylar sheet to act as radiation shield. A comprehensive picture of the whole experimental setup may be obtained from the photograph (P 3.2).

3-3.1b Temperature Calibration

The crystal temperature was calibrated against the temperature displayed by the temperature controller/indicator which actually monitored the temperature of the second cold station to which the hang-down tube was thermally strapped some twelve centimeters
away. This was performed by measuring the susceptibility of \( \text{Mn(NH}_4\text{)}_2\text{(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \) single crystal which is virtually magnetically isotropic and follows Curie law (with \( \theta = 0 \)) down to 1K [4]. Several runs with this crystal were taken for calibration. This showed that at very low temperatures (below ~100K), the crystal temperature differed by about 1K from the temperature of the cold station. Temperature was controlled by the SI controller using a gold-iron (0.07%) / chromel thermocouple as a sensor.

### 3-3.2 Magnetic Anisotropy

The low temperature magnetic anisotropy measurements were carried out from room temperature down to 80K by using a liquid bath type cryostat, designed and fabricated in our laboratory. The temperature within the hang down tube inside the cryostat was maintained steady at any desired level in the temperature range 300 – 80K using a microprocessor based automatic temperature controller supplied by Microwave Corporation, Kolkata. The crystal is suspended inside the hang-down tube of the cryostat. The description of the cryostat is given below.

#### 3-3.2a Cryostat

A schematic diagram of the cryostat is shown in Fig.3.4. The cryostat consists of a wide mouthed double walled glass dewar vessel with a narrow tail to go between the pole pieces of the electromagnet. The inner wall of the vessel is silvered and the annular space is evacuated to
Fig. 3.4
P 3.3 Low temperature anisotropy measurement setup
the order $10^{-3}$ torr. The experimental chamber is a narrow pyrex tube with its lower end made of copper. An insulated heater coil is wound on the lower copper portion of the hang down tube. The hang down tube has a double walled (inner wall silvered) vacuum jacket connected to a vacuum pump through a valve. The cryostat has a flange at the top and is fixed to the base plate with an “O” ring. By adjusting the vacuum inside the vacuum jacket and the current in the heater coil which is controlled by the automatic temperature controller, the temperature inside the crystal chamber is held at any desired value. Liquid nitrogen is pumped in to the dewar from a container as and when required. Low temperature anisotropy setup is also shown in the photograph (P 3.3)

3.3.2b Temperature Sensor

The cryostat chamber temperature was measured using a copper-constantan thermocouple (TC) as a temperature sensor. One of the TC junction is placed inside the experimental tube very close to the crystal and the other junction was kept at ambient temperature. Since a large temperature gradient exists from the base to the top of the tube at room temperature, an appreciable length of the TC leads is wound around the base of the tube to reduce heat conduction through the leads. The ambient temperature was measured by a diode sensor which was calibrated at the triple point of water.
REFERENCES: