

AN IMPROVED METHOD OF MEASURING THE ABSOLUTE SUSCEPTIBILITIES OF SINGLE CRYSTALS OVER WIDE RANGES OF TEMPERATURES

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ABSTRACT. An accurate convenient method has been developed for the measurement of magnetic susceptibilities of single crystals, powders and solutions over wide ranges of temperatures. This is based on the well known Curie method in which various sources of errors have been individually and collectively eliminated to give an accuracy of not less than 0.2%. The present paper gives a detailed description of the balance and a gas-flow type horizontal cryostat for temperature variation. The calibration of the balance and the Cu-constantan thermocouple temperature scale have also been compared against the existing Leiden, Strasbourg and Calcutta measurements, on standard paramagnetic substances, e.g., Cr^{+++} alum, Fe^{+++} alum and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, first two of which are well known to provide the magnetic scale of extreme low temperatures.

INTRODUCTION

A very accurate method for determining the magnetic anisotropy of single crystals, depending on the measurement of critical torque upon the crystals suspended in a homogeneous magnetic field with a fine quartz fibre has already been developed in this laboratory (Dutta, 1953-54, Dutta Roy, 1954). For a complete knowledge of susceptibility behaviours of crystals, the principal absolute susceptibilities also should be measured to the same degree of accuracy. Though by the existing methods of measurements the mean value of the susceptibility has been often determined accurately at a single temperature, no very satisfactory method has yet been evolved for the absolute principal susceptibilities of crystals over wide ranges of temperatures. In the present paper a method has been developed which promises to be very satisfactory for this purpose and applicable universally to crystals, liquids and solutions, over a wide range of temperatures.

THEORY

Most of the absolute susceptibility determinations depend on the measurement of translational force upon the sample placed in an inhomogeneous magnetic field. The general expression for the components of the translational forces on an isotropic sample of volume v , of volume susceptibility k , surrounded by a medium of

volume susceptibility k_0 , along the orthogonal coordinate axes x, y, z , are given by,

$$\left. \begin{aligned} F_x &= (k-k_0) \left(H_x \frac{dH_x}{dx} + H_y \frac{dH_y}{dx} + H_z \frac{dH_z}{dx} \right) v \\ F_y &= (k-k_0) \left(H_x \frac{dH_x}{dy} + H_y \frac{dH_y}{dy} + H_z \frac{dH_z}{dy} \right) v \\ F_z &= (k-k_0) \left(H_x \frac{dH_x}{dz} + H_y \frac{dH_y}{dz} + H_z \frac{dH_z}{dz} \right) v \end{aligned} \right\} \dots (1)$$

If the origin is taken at the geometric centre of the pole gap and x, y , and z , are the directions, from pole to pole in the horizontal plane, perpendicular to this direction in the same plane, and along the vertical, respectively, it is evident that if the pole pieces are so shaped that there is only a field H_x and its gradient $\frac{dH_x}{dy}$, along y , then we are left with only the y -component of the force in the form,

$$F_y = \left(k - k_0 \right) v H_x \frac{dH_x}{dy} \dots (2)$$

For an anisotropic crystalline sample of principal volume susceptibility k_1, k_2 , and k_3 , inclined to H_x at angles whose direction cosines are l, m, n , the force is given by

$$F_y = \left\{ (k_1 l^2 + k_2 m^2 + k_3 n^2) - k_0 \right\} v H_x \frac{dH_x}{dy} \dots (3)$$

which further simplifies to

$$F_y = (k_1 - k_0) v H_x \frac{dH_x}{dy} \dots (4)$$

if the crystal is placed with its k_1 direction along H_x .

In addition to these translational forces there are also component couples on the crystal about the coordinate axis tending to rotate the crystal in such a manner as to place the maximum direction of susceptibility along the magnetic field.

The situation is further complicated by anisotropic Poisson distribution of magnetization over the surface of the crystal, including the demagnetisation factor in an initially homogeneous field and consequent couples. The surface forces are proportional to $(k-k_0)^2$ and is therefore extremely small under normal circumstances.

Experimental arrangements usually have to be so devised that the rotatory tendencies are eliminated and the translatory motion is made unidirectional along one of the coordinate axis, say y , as in the case already considered.

SUMMARY OF THE EXISTING METHODS

Various methods of measuring magnetic susceptibility, based on the measurement of force on a body placed in a non-homogeneous magnetic field, have been developed from time to time and are essentially variations or modifications of the well known methods of Gouy or of Curie. The Gouy method, which is very sensitive and convenient for absolute susceptibility measurement, usually requires a large amount of the substance in the form of a long cylindrical rod of uniform cross section or finely powdered and packed inside a long glass tube. But most of the crystalline solids are magnetically anisotropic and may give rise on packing to an orientation effect of the finely powdered crystallites, particularly in a magnetic field. Further, large amount of the substance is necessary and the method is not suitable for observation over a large temperature range. The Curie method allows quick relative measurements on small amounts of powder or solution specimens and is very adaptable for low and high temperature measurements and may be adapted for anisotropic crystals. But these advantages are offset to a great extent by the difficulty of placing the substances always in a standard position in the field. To eliminate this uncertainty several workers [Fereday, (1931) Foex-Forrer (1926), Sucksmith (1939)] have designed shapes of pole pieces in which maximum $H_x \frac{dH_x}{dy}$ remains constant over an appreciable region. In Foex-Forrer balance the magnetic force is compensated by the electrodynamic force exerted between a current-bearing coil carried on the moving system and a fixed permanent magnet. The balance suspension arrangement, however is extremely cumbersome, gravitation being the main restoring force, the deflection sensitivity is rather low, and stray fields troublesome. Sucksmith ring balance which has been developed by Jackson (1933) for measuring the susceptibility of powders as well as for crystals, is not suitable for small susceptibilities. Quartz microbalance as developed by Bose (1947), is very suitable for low and room temperature measurements for both powders and crystals, but is unsuitable for high temperature owing to convection disturbances. None of these methods can claim more than an overall accuracy of 1%. Further serious uncertainties, which is common to all methods, are the impurities and imperfections and inaccurate setting of crystals for which special care should be taken.

The present is an adaptation of Curie method in which the various sources of errors have been individually and collectively sought to be removed to a large extent, with further scope of improvement which, when done, should make the method unrivalled for reliability.

DESCRIPTION OF THE BALANCE

The balance (Figure 1), essentially consists of a light horizontal torsion arm *A* made of thin walled pyrex glass tubing. This is suspended at the centre from one end of a fine vertical quartz fibre *F*, the other end of the fibre being attached to a torsion head *H*. The torsion head is mounted on the top of an

1" wide glass tube through which the fibre passes. The glass tube is fitted leak-tight to the balance box *S* and to torsion head by conical metal fittings attached with hard sealing wax. One extremity of the balance beam passes out through

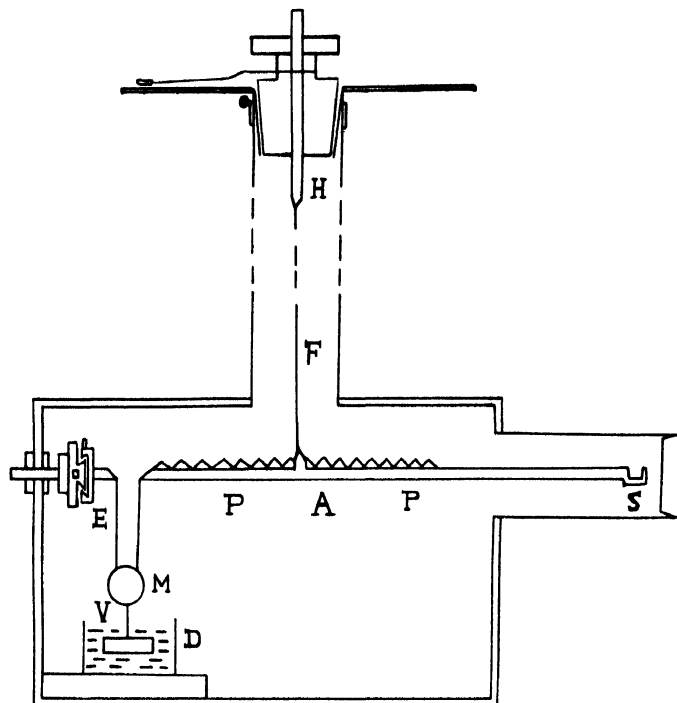


Fig. 1—A sketch of the balance.

a hole on the side of the balance case, to which an extra length of rod is attached, going into the inhomogeneous magnetic field, at the end of which the sample S_1 is mounted. The protruding end is protected from draught and contamination by glass tube fitted by conical metal coupling to the case. At the other end of the beam a sensitive Kelvin bifilar suspension mirror M is attached, to magnify the movement of the beam as well as to provide a sufficient controlling couple upon the system. The dashpot P contains kerosine oil in which four mica damping vanes V hang. The pin E is attached to a miniature three dimensional adjustment stage for the bifilar suspension, consisting of a cross slide which can also be moved at right angles to the plane of the slides, and may be adjusted to obtain maximum sensitivity and stability of the system. The brass case S , which surrounds the torsion arm and suspended mirror, is mounted upon a stand, with two horizontal cross slides and is also capable of rotation and up and down motion telescopically for the correct adjustment of the position of the sample in the magnetic field. The base of the stand is mounted upon three levelling screws and the whole thing is placed upon a thick marble slab built into the wall of the room. The front of the case has a sliding glass plate through which observations are made; the edges can be made leak-tight with

plasticin. To obtain horizontality of the balance arm when different masses of the substance are used, two scale pans P, P , are attached to the beam within the balance case on which suitable weights are placed. To keep constant loading on the beam always, the final balancing is obtained by taking off load on the arm on the same side of the specimen. Fine adjustments are made by shifting a rider along the beam to which a long thin serrated strip, of mica, is attached for the purpose. The verticality of the suspension fibre and the horizontality of the beam are separately tested by comparison with a fine plumb line of quartz fibre, observed through a low power telescope with circular scale and pointer and fitted with a fine cross-wire. The displacement of the substance on applying the magnetic field, as observed by the movement of the image of a fine glass scale reflected from the bifilar mirror through moderate power telescope, is usually several centimetres. By giving suitable torsions to the suspension fibre by means of the vernier torsion head reading to 10^{th} of a degree, the balance beam is brought back accurately to its original position. In order to rotate the torsion head without causing vibrations of the system, and also to enable the same operator, looking through the telescope from a distance of about two metres (an order to have a high optical magnification), to work the torsion head, this is coupled by a slow gear arrangement and flexible shaft to a small motor which can be reversed, if necessary, with switches close by the observer. The beam, when not in use, may be arrested by a spring catch, and operated from outside by lever mechanism. The interior of the balance may be illuminated for the preliminary adjustments with a small electric lamp (6 volts) inside the casing. The balance is shown in figure 1(a).

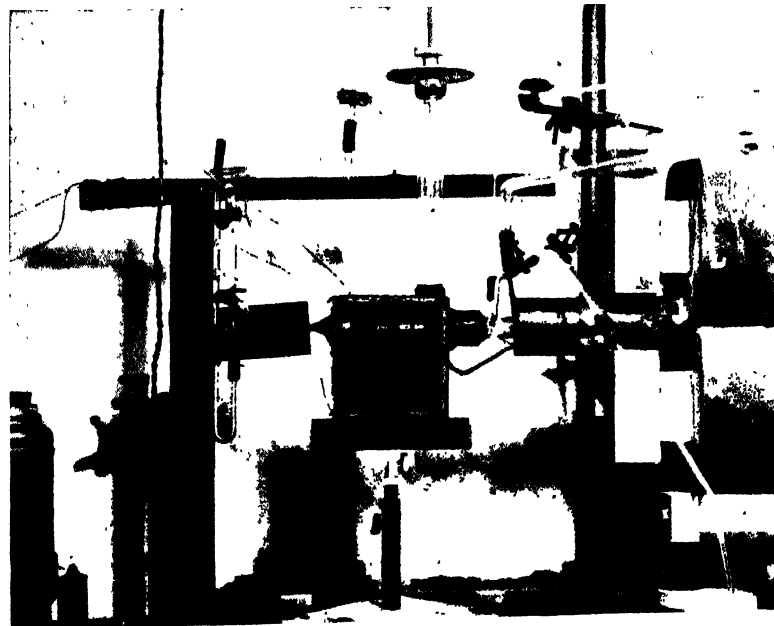


Fig. 1(a)

(a) *Use of vertical field.*

The balance may be conveniently used for measurement of powders and solutions using a horizontal field. If it is desired to measure the principal susceptibility of a crystal, a horizontal field is inconvenient. It would be well nigh impossible to set the crystal with its principal susceptibility direction along the field by trial. So either a series of readings have to be taken by rotating the crystal or the magnet (Hupse, 1942) or by having a flexible suspension (Bose, 1947) so as to let the crystal freely set by itself in the field. But these are attended by great practical difficulties. We have altogether avoided these difficulties by having a vertical field and horizontal gradient. This is simply obtained by turning over our electromagnet on one side with its pole-pieces one above another. The magnet is mounted upon a circular rotating base with three levelling screws and a spirit level so that it may be rotated about a vertical axis and the edges of the pole pieces made accurately vertical in the final position.

(b) *Shaping the gradient*

Designing of pole pieces for the gradient are very carefully done so that at each different current the force $H_x \cdot dH_x/dy$ remains constant over wide regions. Various workers have used special types of pole pieces to obtain the above condition as already mentioned. Sucksmith shape appears to be the simplest and as

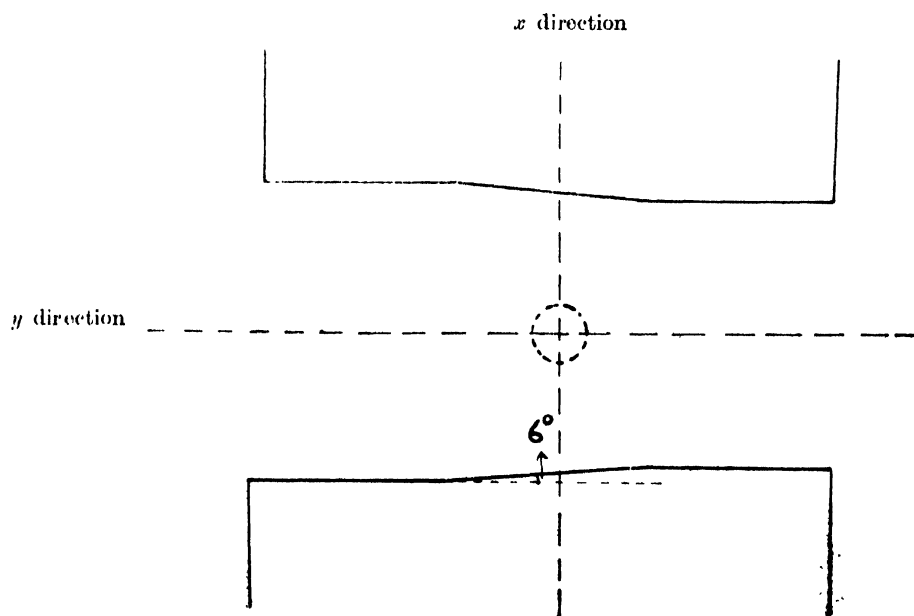


Fig. 2.—Arrangement of the pole faces, section to normal to z direction

effective as any other. We have adopted this with suitable modifications to fit our values of magnet current, pole gap, face area etc., made from theoretical considerations and through experimental checking. To obtain the desired gradient of

the field, a pair of thick rectangular pieces of soft iron, fitting flat on the original large rectangular parallel pole pieces (pole gap 2.5 inches) of our electromagnet, are each marked lengthwise (y direction) into three equal sections. The three sections are then shaped as shown in the figure. 2 below, so that the middle section is inclined at about 6° to the end ones. The best angle is obtained after several trials with slightly differing angles. These pole-shoes are fixed to the original pole-pieces with small soft iron pins near the edges.

The trials consisted of graphical plotting of the force exerted on a paramagnetic sample in the field, at different accurately measured positions within the pole gap, for each of the differently angled pole shoes. The forces are most conveniently measured by the balance already described. For the purpose of plotting absolute forces are not necessary. The angles of torsion proportional to forces can be measured with an accuracy of not less than 0.1%. Temperature is kept constant during each set of measurement. Some typical results are shown in the graphs.

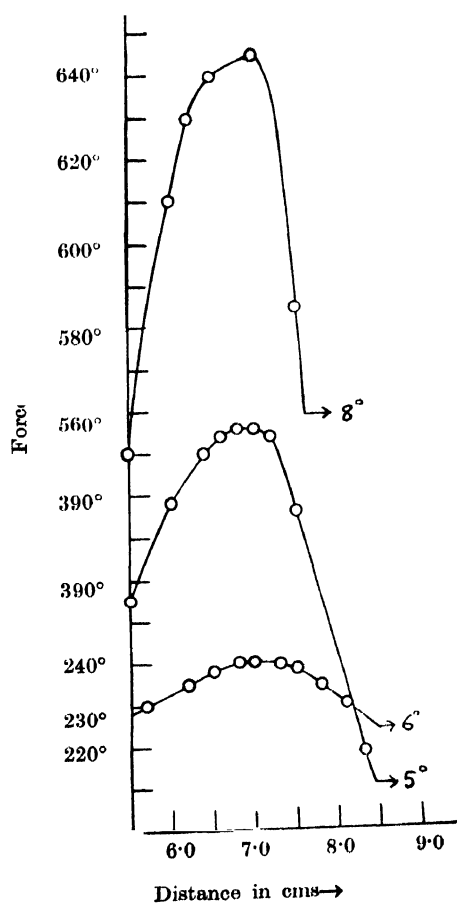


Fig. 3.—Force-distance curves with different pole gradients.

The best constancy of the force about .05% is obtained with the 6° poleshoes, with a magnet current 1.4 ampere over a volume 0.5 cms³. Our crystals or other specimens never exceeded this size.

(c) *Mounting the specimen*

The crystal is always placed accurately at the centre of the studied constant maximum region of force between the shaped pole pieces. This is done by having two pieces of graph paper pasted on to two sides of the pole pieces at right angles, marked for the said region, and locating the position of the crystal with reference to these through a telemicroscope from two different positions. The suspension of cubic crystals, powders and solutions is very easy as the question of anisotropy does not arise and is done very conveniently by placing the sample (in the case of solutions and powder samples are packed within a glass container) at the end of a sufficiently long thin glass rod which is formed into a loop to take the sample. The other end is inserted into the hollow beam of the balance and fixed

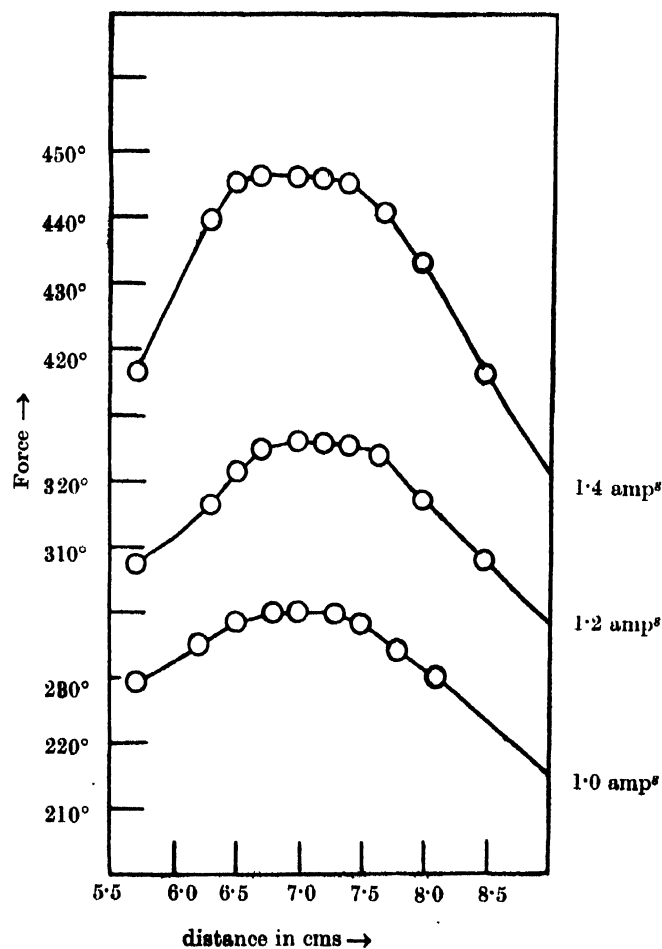


Fig. 4.—Force distance curve with a particular pole gradient with different currents

with durofix cement. But in the measurement of principal susceptibility along a known direction in a crystal, it is attached with durofix to the long rod (without loop) with the desired direction normal to the length of the rod, then the rod is rotated until this direction is vertical and then fixed permanently with durofix. The verticality can be ascertained very accurately by comparison with a fine plumb line, by means of a telemicroscope.

CURRENT CONTROL

The experimental work is done at low values of magnet current usually 1 amp. to 1.4 amps. We have not used any special device for automatically stabilising the magnet current except that we have taken the current from a compound wound D. C. generator, instead of directly from our 6-phase rectified D. C. mains which fluctuate rather badly, and also relied upon the high inductance of the magnet to stabilise the current further. The low values of current also produces no heating effect on the magnetization of the core. Moreover, the current can be accurately adjusted with a fine controlled rheostat and an accurate Weston ammeter viewed through a low power microscope.

CALIBRATION OF THE BALANCE

When the unknown sample of volume v placed in air (k_a) has been restored to the original position in the field by twisting the quartz fibre through an angle θ , against the magnetic force, and the corresponding angle of twist for the standard substance (of volume v_s , not very different from v and both smaller, than volume over which $H_x \frac{dH_x}{dy}$ is constant) in the same mean position, same field and at the same temperature is θ_s , we have from equation (4)

$$\frac{\theta}{\theta_s} = \frac{k - k_a}{k_s - k_a} \cdot \frac{v}{v_s} = \frac{m}{m_s} \cdot \frac{\chi - \frac{k_a}{\rho}}{\chi_s - \frac{k_a}{\rho_s}} \quad \dots (5)$$

where m and m_s are the masses, ρ and ρ_s the densities and χ and χ_s the mass susceptibilities of the unknown and standard substance respectively.

$$\chi = \frac{\theta}{\theta_s} \cdot \frac{m_s}{m} \left(\chi_s - \frac{k_a}{\rho_s} \right) + \frac{k_a}{\rho} \quad \dots (6)$$

where $k_a = 0.028 \times (300/T)^2 \times 10^{-5}$ at T° absolute.

As primary standard substance, we have taken aqueous NiCl_2 solution the mass susceptibility of which has been measured very accurately by a number of workers. For NiCl_2 at 20°C the values of gm. mol. susceptibility $\times 10^6$ are 4411 by Weiss and Bruins (1926), 4423 by Brant (1921), 4423 by Bose (1926), 4400 by

Nettleton and Sugden (1939). The mean value is 4431. On the basis, that the effective moment of Ni^{++} does not change with concentration and with small variations of temperature near 300°K , as observed by the above workers, the susceptibility of isolation per gram is given by the formula

$$\chi \times 10^6 = \left(\frac{10160}{T} + 0.7193 - 0.486 \right) C - 0.7193 \quad \dots (7)$$

where C = the conc. of solution in grams of NiCl_2 per gram of solution.

T = the absolute temp. χ_w for water at $20^\circ\text{C} = 0.7193 \times 10^{-6}$.

The solution used by us made from A. R. quality of E. Merck is free from cobalt, dissolved in double distilled water having $C = 0.2590$ and density at $305.8^\circ\text{K} = 1.2993$.

The reliability of performance of the balance, including accuracy, stability, reproducibility, sensitivity etc. is checked in the following manner.

(a) Ferric alum crystal grows in cubic class as regular octahedron so that it has neither magnetic anisotropy nor appreciable shape effect. A carefully purified and well grown crystal weighing 0.04080 gms. is carefully mounted at the end of the balance arm, centred carefully in the region of constant H_x , dH_x/dy and the torque due to magnetic field upon the system is exactly balanced by slowly twisting the fibre, observing the image of the zero of the illuminated scale through the telescope. The angle of torsion necessary for this purpose is corrected for the force upon the arm alone. The temperature is noted accurately. The torsion head is restored to its initial position, and the field is switched off. No appreciable zero shift is generally observed. The same operations are performed with a pyrex glass ampoule filled with a weighed quantity of standard NiCl_2 solution. Here correction has to be made for the empty ampoule. The relevant data necessary for the calculation of mass susceptibility of the alum is given in Table I, for one typical case. The diamagnetic corrections are made from Stoner. Measurements with five different crystals were made. The standard reading is repeated every time. Any small temperature fluctuation during these experiments is noted and corrected for. The individual readings do not differ from the mean by more than 0.1%. The value of the effective magnetic moment p_{eff}^2 is found to be 35.08 at 300°K which is a little more than $\frac{1}{2}\%$ greater from the value obtained by Onnes and Oosterhuis, (1926), well within the limits of accuracy of these authors. It has been, however, shown by Van Vleck and Penney (1934) that Fe^{+++} ion which is in ${}^6S_{5/2}$ state, the mean susceptibility, should obey a Curie law strictly upto $1/T^2$ terms at least. The 'spin only' value for the mean square moment is then 35.04 which is a little more than 0.1% smaller than our values and just within the conservatively estimated limit of error about 0.2% of our experiment. Terms of higher order than $1/T^2$ might introduce a very small departure from spin only value. But the present results are not able to point to it.

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(b) Chromium potassium alum also grows in cubic class in the form of regular octahedron. Crystals were prepared from carefully purified samples of the salt and magnetic measurements performed with NiCl_2 solution as standard, in a similar way as above. The final value for the susceptibility is the mean for at least five crystals and is given in Table I. The value for mean square of the effective moment is 15.05 which may be compared to the earlier values 14.80 by de Haas and Gorter (1929) and 15.05 Mmc. Serres, (1932). Since Serres has shown that Leiden data suffered from errors in calibration, and agreed very well with her own value after necessary corrections, we have quoted only these values in Table I, which agree with our own to within less than 0.1%. It is possible that for the same reason Leiden value for Fe^{+++} alum quoted earlier is less than ours. Our values for Cr^{+++} are definitely higher by 0.3% than the spin only value of 15.00.

(c) To check the reliability and reproducibility of our measurement further we have measured the sample of Fe^{+++} alum against a different sample of Cr^{+++} alum as secondary standard, taking 15.045 as the value of mean p_{eff}^2 . The relevant data are given in the table. The value of Fe^{+++} alum comes out as 35.09, to within 1 part in 3500 of our previous value.

(d) As a last check of our method, applied to anisotropic crystals, we have measured a crystal of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal) along its tetragonal axis. The crystal grows as di-tetragonal pyramid and has little anisotropy of shape for a well grown crystal. The value of p_{eff}^2 is found to be 9.768 as against 9.736, a careful measurement by Mookerji (1946), using a modified Rabi method of high sensitivity, a difference of 0.3% within the limits of error of Mookerji.

Further details of rigorous tests of the balance in the low temperature range and a comparison of our thermometric scale with Leiden standard is given in the next section.

THE CRYOSTAT AND LOW TEMPERATURE MEASUREMENT

For accurate low temperature measurements of magnetic susceptibility, a suitable gas flow type cryostat (horizontal) has been constructed. The new cryostat is a modified design of that already in use in our laboratory (Bose, 1947). The cryostat consists of a double walled chamber closed at the bottom with thin copper sheet 5.5" length 2.4" outer diameter $\frac{1}{4}$ " interspace between the walls. Inner space is packed with fine copper wire gauze through the centre of which passes the experimental tube of thin copper 1" in diameter closed at the bottom. The annular space between the walls is connected by a stainless steel capillary tube $\frac{1}{4}$ mm inner diameter to a mercury manometer system and serves as a constant volume air thermostatic control unit. Two platinum contacts, one at the surface of mercury, the other inside mercury are

TABLE 1

Comparison of p_{eff}^2 for the F_e^{+++} and C_r^{+++} alum and $NiSO_4 \cdot 6H_2O$.

Mass and density of the substance with corresponding rotation on torsion head		Mass susceptibility		p_{eff}^2 in Bohr magneton units at 300°K	
Standard Substance	Unknown Substance	$\chi_g \times 10^6$	$\chi_m \times 10^6$	Present Value	Earlier Value
NiCl ₂ $m=0.12140$	Fe ⁺⁺⁺ alum $m=0.04080$	7.9287 at 306.4 °K	28.94 at 306.4 °K	35.08	35.04 Spin only value, 34.89 (Onnes and Oosterhuis).
$\rho=1.2998$ $\theta=227.4^\circ$	$\rho=1.724$ $\theta=284.9^\circ$				
NiCl ₂ $m=0.12140$	Cr ⁺⁺⁺ alum $m=0.08500$	7.9287 at 306.4°K	11.715 at 306.4°K	15.04	15.05 (de Haas & Gorter as corrected by Serres), 15.06 (Serres), 15.00 (Spin only).
$\rho=1.2993$ $\theta=227.4^\circ$	$\rho=1.842$ $\theta=235.6^\circ$				
Cr ⁺⁺⁺ alum $m=0.12100$	Fe ⁺⁺⁺ alum $m=0.04080$	11.91 at 300.70°K	29.51 at 300.7°K	35.09	
$\rho=1.842$ $\theta=80.5^\circ$	$\rho=1.724$ $\theta=67.3^\circ$				
Cr ⁺⁺⁺ alum $m=0.12280$	NiSO ₄ ·6H ₂ O (along axis) $m=0.15200$	11.65 at 307.0°K	14.555 at 307.0°K	9.768	9.736 (Mookherji).
$\rho=1.842$ $\theta=120.8^\circ$	$\rho=2.080$ $\theta=186.6^\circ$				

connected in the usual way to a magnetic relay breaking and making a suction pump motor circuit. The top of the chamber is closed by a german silver cup through which the experimental tube, upper part of which is made also of german silver, and two other stainless steel pipes of 2mm diameter, pass out. Of the two pipes one goes to the bottom of the chamber and is connected outside by a soft cork coupling to one end of a vacuum-jacketted pyrex glass tube carrying cold gas from the refrigerant storage chamber. The other pipe, which is cut short below the cryostat top, is connected to the suction pump through a large pressure stabilizing bottle and carries the exhaust gas from the cryostat chamber. The refrigerant chamber is a german silver cylindrical vessel closed at both ends kept within a wide mouthed thermos bottle and contains liquid oxygen. The level of liquid oxygen is indicated by a glycerine pressure gauge and can be replenished through a tube at the top of the chamber usually kept closed with a cork. Atmospheric air dried by a dehydrating tower is cooled by passage through a copper spiral immersed in liquid oxygen, and is sucked into the cryostat chamber through the vacuum line by

the suction pump. While passing through the wire gauze packing of the chamber the current of cold air comes into intimate contact with the large highly conducting surface area of the gauze, and is effectively deprived of cold. The turbulent flow as also the high conductivity of the material causes a good uniformity of temperature over a large portion of the chamber. Uniformity of temperature and conservation of cold are further improved by suitable adjustment of thermal capacity of chamber and enclosing the whole within a silvered pyrex cylindrical Dewar vessel which is protected from breakage by a metal casing. The german silver part of the experimental tube is coupled with durofix cement to the glass tube attached to balance case, through which the balance beam passes into the experimental tube.

The thermostatic relay system is preset to a given low temperature. When this is reached, the relay switches off the pump. The small heat leakage into the system tends to raise the temperature and the relay switches on the suction pump again and temperature may be maintained fairly accurately constant. For extremely fine control, a controlled leak is introduced on the pump side, by adjusting which and also the speed of the pump by a rheostat the heat leak from outside may be accurately balanced by the continuous cold in-flow carried by the circulating gas, and the temperature control to within 0.01°K may be achieved. For quicker work, where less sensitivity is required, the cooling spiral in refrigerant chamber is dispensed with and liquid air in controlled quantities may be directly sucked in the cryostat chamber, allowed to evaporate at the bottom of the chamber and circulated through the system as before.

Evidently the cryostat has to be set up in a horizontal position so as to go between the pole pieces of the magnet placed on its side with one pole above another as already mentioned.

Low temperature measurements of susceptibility requires a little modification in the room temperature use of the balance. A stop for the beam has to be placed at the outlet in the balance case so that the specimen may not come in contact with experimental tube and stick there. Another trouble in the measurement of the balance at low temperature arises from deposition of moisture on the cold part of the beam. This is prevented by making all fittings of the balance case leak-tight with durofix and plasticin and not only keeping a strong dehydrating agent within the balance case but also washing inside with dry air from an elaborate dehydrating tower system before the low temperature run is started.

TEMPERATURE MEASUREMENT

The temperature is measured with an accuracy of 0.1°K with a copper-constantan thermocouple, the E.M.F. being measured in the usual manner with a Leeds Northrup potentiometer reading to 2 microvolts. The thermocouple is calibrated at the usual standard low temperature points and also against one

calibrated earlier by Bose (1947) and checked from time to time. Our thermocouple shows a systematic deviation from the earlier one, which is no doubt due to differences in composition and history of the couple. For this reason we wanted to make a check for the calibration of our couple. This is done by taking magnetic susceptibility measurements on substances well known to obey Curie law to the degree of accuracy derived in the relative susceptibility and temperature measurements on Leiden scale on these substances. Two such convenient substances are ferric ammonium alum and chromium potassium alum, and we have measured the mean susceptibility of these as before. The formula used by us is

$$\frac{F_T}{F_\theta} = \frac{\chi_T}{\chi_\theta} \left[1 + \frac{k_{a\theta}}{k_\theta} \left(1 - \gamma\theta \right) \left(1 - \frac{\theta}{T} \right) \right] \quad \dots (7)$$

where χ_T , and χ_θ are the gram. molecular susceptibilities of the crystal at temperature T and room temperature respectively, and F_T and F_θ are the forces acting on the crystal at these temperatures, $k_{a\theta}$ and k_θ are the volume susceptibility of air and that of the crystal at room temperature θ , and γ is the coefficient of thermal volume expansion of the crystal.

The results as compared to those of earlier workers are given below.

TABLE II
Temperature variation of the gm. molecular susceptibility of
 $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 24\text{H}_2\text{O}$

Onnes & Oosterhuis			Present Author		
Temp °K (Leiden scale)	$\chi_M \cdot 10^6$ (room temp. value corrected by us.)	p_{eff}^2	Temp °K (Our scale)	$\chi_M \cdot 10^6$	p_{eff}^2
290.0	15010	35.07	300.5	14470	35.08
169.6	25370	34.70	278.8	15600	35.06
77.1	56040	34.83	242.0	17980	35.07
			222.1	19670	35.05
			195.5	22110	34.84
			179.2	24090	34.81
			171.2	25170	34.74
			147.8	29360	34.83
			133.2	32570	34.97
			121.0	35880	35.00
			99.0	43740	34.91

TABLE III
Temperature variation of the gm. molecular susceptibility of
 $\text{Cr}_2 \cdot (\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$.

de Haas & Gorter (Corrected by Serres)			Serres			Present author		
Temp.°K (Leid. Scale)	$\chi_M \times 10^6$	p_{eff}^2	Temp.°K (Inter. Scale)	$\chi_M \times 10^6$	p_{eff}^2	Temp.°K (Our Scale)	$\chi_M \times 10^6$	p_{eff}^2
290.0	6437	15.05	292.2	6377	15.05	305.0	6119	15.04
169.7	10980	15.02	292.0	6385	15.03	299.5	6317	15.05
143.6	12960	15.00	291.2	6403	15.03	272.0	6792	14.90
77.7	24010	15.04	89.7	20708	14.97	247.0	7457	14.91
						230.4	8019	14.90
						227.6	8098	14.87
						212.0	8710	14.90
						200.0	9204	14.85
						199.5	9226	14.86
						170.3	10910	14.98
						169.7	10940	14.99
						158.0	11800	15.03
						157.4	11810	15.00
						146.0	12740	14.99
						138.0	13490	15.01
						132.1	14020	14.93
						113.5	16320	14.95
						103.8	17800	14.90
						102.0	18170	14.94
						101.0	18290	14.90

The values of p_{eff}^2 when plotted against T should give a straight line parallel to T -axis for substances obeying Curie law exactly. Such a graphical presentation is extremely sensitive not only to experimental errors but also to small departures from ideal Curie law. On plotting all the values for Fe^{+++} alum in a single graph (figure 5) we find that all the three available Leiden values at three different temperatures after correction for the room temperature values as indicated earlier, fall exactly on the same curve as our results. This value as indicated not only values of Leiden in agreeing with ours, are more accurate than their room temperature value, but also our measured temperatures fit perfectly well with the Leiden scale. It is very unlikely that errors in susceptibility and temperature measurements happened to be in opposite directions at all the comparison temperatures so that an accidental fit has been obtained.

In further support as to evidence against such a chance, we have our p_{eff}^2 -versus- T curve for Cr^{+++} alum (figure 6). Serres', de Haas and Gorter's values for this salt again fit in quite well with our curve. All these data are thus additional evidence for the accuracy and reliability of our methods of measurement of susceptibility as well as temperature.

It is of some interest to note that our curve for Fe^{+++} alum shows a small departure from Curie law, by a deviation from linearity and a minimum at about 170°K . This deviation is reproducible for different samples of crystals and is reversible with temperature. It was already noticeable in the Leiden measurement, but was not given any significance. Our curve being plotted for a large number of successive temperatures, shows the effect very well, and without any doubt.

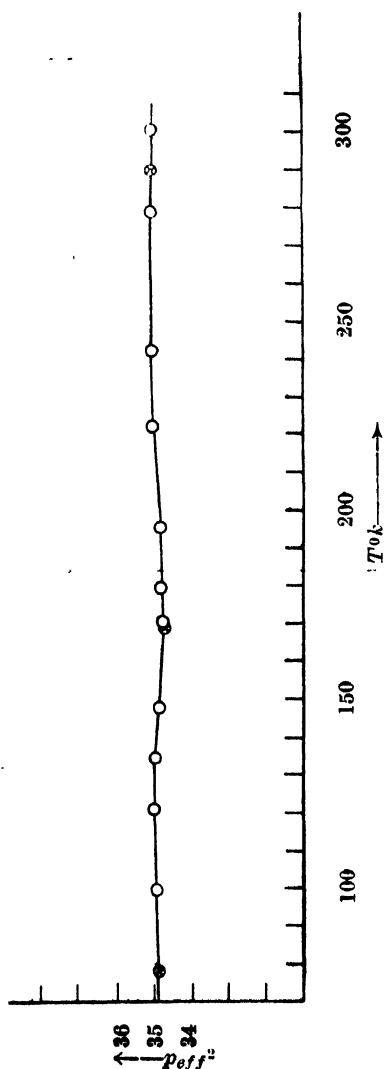


Fig. 5.— p_{eff}^2 — T curve for ferric alum.

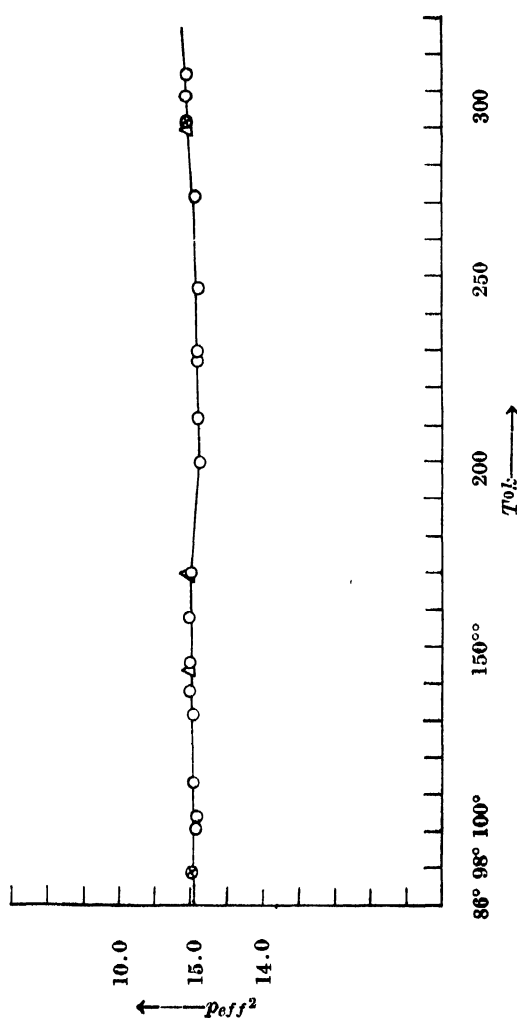


Fig. 6.— p_{eff}^2 — T curve for chrome alum.

Cr^{+++} alum also shows a similar noticeable change at about 200°K . These departures are evidently due to some small thermal changes in the internal structures causing changes in the electric fields in the crystals, similar to those observed

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by Bose, Mitra, and Datta in Cu^{++} and Ni^{++} salts (in course of publication). A study of the magnetic behaviours of a large number of alums of the iron group has been completed by the present method, and will be discussed in details in future communications.

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REFERENCES

- Bose, A., 1935, *Proc. Ind. Acad. Sci.*, **1**, 606.
Bose, A., 1947, *Ind. Jour. Phys.*, **21**, 277.
Curie, P., 1895, *Jour. de Phys.*, **4**, 187, 263.
de Haas, W. J. and Gorter, C. J., 1920-31, *Comm. Leiden.*, no. 208 c.
Datta, S. K., 1953, *Ind. Jour. Phys.*, **27**, 155.
Datta, S. K., 1954, *Ind. Jour. Phys.*, **28**, 239.
Dutta Roy, S. K., 1954, *Ind. Jour. Phys.*, **28**, 183.
Fereday, R. A., 1931, *Proc. Phys. Soc.*, **43**, 383.
Foex, G. and Forrer, R., 1926, *Jour. de Phys.*, **7**, 180.
Jackson, L. C., 1933, *Proc. Roy. Soc., A* **140**, 695.
Brant, L., 1921, *Phys. Rev.*, **17**, 678.
Hupse, J. C., 1942, *Physica*, **9**, 633.
Mookerji, A., 1946, *Ind. Jour. Phys.*, **20**, 9.
Nettleton, H. R. and Sugden, S., 1939, *Proc. Roy. Soc.*, **178**, 313.
Onnes, H. K. and Oosterhuis, E., *Comm. Leiden.*, no. 139c.
Rabi, I. I., 1927, *Phys. Rev.*, **29**, 174.
Serres, A., 1932, *Ann. d. Phys.*, **17**, 551.
Stoner, E. C., *Magnetism and Matter*, (1934, Methuen, London).
Sucksmith, W., 1939, *Proc. Roy. Soc.*, **17**, 551.
Van Vleck, J. H., and Penney, W. G., 1934, *Phil. Mag.*, **17**, 961.
Weiss, P. and Bruins, T. L., 1926, *Proc. Amst. Acad.*, **18**, 246.