A CONVENIENT AND SENSITIVE BALANCE FOR MEASURING MAGNETIC ANISOTROPIES OF SINGLE CRYSTALS

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ABSTRACT. For measuring magnetic anisotropies of single crystals a new sensitive balance has been described. The instrument incorporates electrodynamic method of balance ing the couple experienced by a crystal and is operated electrically from a distance. Elimination of manual handling of the balance ensures high reproducibility and operational convenience. It is well adopted for low temperature work. The performance of the balance is thoroughly tested and discussed.

INTRODUCTION

The past few decades have witnessed a sharp rise in interest in the magnetic properties of single crystals. Studies on the diamagnetic organic crystals by Krishnan and Banerji (1935, 1938), Banerji (1938) and recently by Mookherji *et al* (1959, 1961) show the close correlation between the magnetic anisotropy and the molecular and crystal structure. In understanding the nature of the ligand fields in the single crystals of the transition metal ions, the magnetic anisotropy and its variation with temperature play a very fundamental role. Extensive investigation on the crystals of the iron group elements undertaken by Bose and co-workers (1961, 1963) points to the sensitive field dependence of the magnetic anisotropy and its thermal variation. Also, in the case of the rare-earth ions where the electrons responsible for giving rise to paramagnetism, are partially shielded by closed shell of outer electrons, the studies of Neogy (1963), Neogy and Mookherji (1965) show the significance of anisotropy for correct determination of the crystal field parameters. Because of this pivotal importance of the magnetic anisotropy we are faced with the problem of collecting a large amount of data of fairly high standard on this physical property. To ensure a fast process for doing the same, it is very necessary, that a simple and very sensitive method be evolved to take the drudgery out of the existing methods for measuring anisotropy.

A quick survey of the present methods of measuring magnetic anisotropy shows that there are only three of them to be taken notice of. Out of these, the oscillation method has long been discarded as being rather crude. The only

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two widely used techniques are the well-known Krishnan and Banerji s spin method and later developed Stout and Griefel's (1950) null method. The details of these two methods are available in the original literature and it will suffice to point out here that both the procedures require manual handling of the delicate suspension system which is rather inconvenient and puts undue physical strain on the worker. Furthermore, the spin method involves determination of torsional constants of the quartz fibres which is not very easy to handle and at low temperature when the anisotropies of paramagnetic crystals increase manyfold their room temperature value, the sudden violent spinning often becomes a problem. In the Stout and Griefel method if torsional constant of the fibre is small, there may be appreciable error in fixing the zero position after the crystal is rotated through 45° or any other angle due to the small residual magnetic field. This error may, however, be avoided if the magnet is rotated through the fixed angle instead of the crystal and this incidentally does away with the necessity of using a hexagonal mirror. The accuracy of these methods can obviously be increased by the use of large well-calibrated torsion head as is often done, (Guha Thakurta *et al*, 1966). A highly suitable yet very simple way to get around the difficulties, is the electrodynamic method of balancing the couple experienced by the crystal in the Stout and Griefel method. This eliminates all kinds of direct manual operation on the suspension system and also, since the restoring couple is not furnished by the application of torsion to the suspension fibre, it is no longer necessary to use delicate fibres for this purpose. The description of the balance is given in the next section. The linearity of values obtained for crystals of different masses and also for different sin 2θ values, where θ's are the angles of rotation of the magnet, is examined. Some crystals which are usually held as standard for magnetic field calibration work are also measured using $CuSO_4.5H_2O$ as standard and the values are compared with those of previous workers.

DESCRIPTION OF THE BALANCE

A schematic diagram of the balance is shown in fig. 1. Essentially, it may be looked upon as a modified form of a suspended coil galvanometer. The balance coil (5) is wound upon a light rectangular aluminium frame attached to a thin glass rod (20) carrying a small plane mirror (19). The coil is suspended by means of a pyrex fibre (2) from a small torsion head (1) and is free to move in the radial field of the local magnet (6). The two leads of the coil are brought out by means of two phosphorbronze spirals (4) attached to the coil. The spirals are wound in opposite directions to nullify any rotational effect on the suspension system due to the thermal expansion of the spirals, owing to temperature fluctuations during the course of measurement. A sufficiently long glass rod (9) is rigidly attached to the lower end of the glass rod carrying the coil. A small glass hook (11) is fixed to the free end of the long glass rod. The crystal (13) to be studied is attached to

another very thin glass rod (12) with a hook at one end; the length of the rod is so adjusted that when it is suspended from the upper hook, the crystal comes just at the centre of the pole gap of the rotatable electromagnet (14). A heavy glass bead (10) is fixed to the rod (9) to increase the stability of the system against

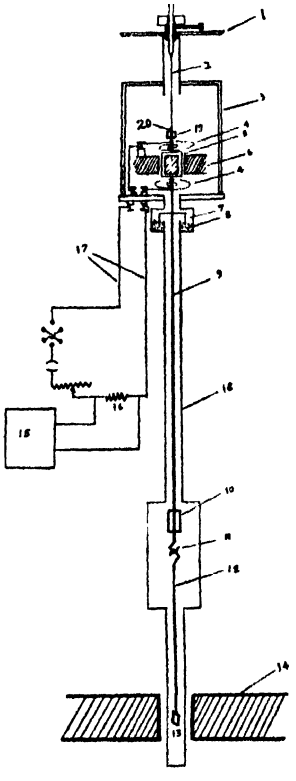

Fig 1

Figure (1)—(1) Torsion head. (2) Pyrex fibre. (3) Perspex case. (4) Phosphorbronze spirals. (5) Aluminium frame. (6) Permanent Magnet. (7) Oil-sealing glass cup. (8) Watch oil. (9) Glass rod. (10) Glass bead. (11) Glass hooks. (12) Very thin glass rod for crystal suspension. (13) Crystal. (14) Pole-pieces of rotatable electromagnet. (15) Potentiometer. (16) Standard resistance. (17) Coil leads. (18) Outer casing. (19) Plane Mirror. (20) Glass rod.

disturbances during the process of changing specimens to be measured. The light spot deflected by the mirror is detected by a differential phototube arrangement.

The balance may easily be adapted for low temperature work with the introduction of an oil-sealing mechanism '7' and '8' which hermetically separates the crystal chamber from the upper part of the balance and thus prevents the humidity from entering the balance box.

MEASUREMENT OF CURRENT

As the couple experienced by the crystal is proportional to the square of the magnetic field it is essential that the latter should be maintained strictly constant.

The change in the magnetic field due to small variation in the coil current is avoided by using an electronically regulated power supply capable of maintaining the current within 0.05% of the desired value up to 5 amperes. For fine adjustment of the current a screw motion rheostat is connected in series with the magnet. The constancy of the current is checked by means of the arrangement showing in fig. 2 wherein the voltage drop across a standard resistance (1) is balanced by the potentiometric arrangement shown. It is not necessary to measure the actual voltage drop across (1) : the constancy of this voltage drop is essential. The absence of any deflection in the galvanometer (3) ensures this constancy. The current in the potentiometer circuit is checked from time to time by means of the standard cell (2). This arrangement is sensitive enough to give a deflection of 10 cm, in the 'Multiflex' galvanometer for 1 mA change in the coil current.

OPERATION

The procedure adopted to align the direction of the maximum susceptibility of the crystal in the horizontal plane with the magnetic field direction, is similar to that of Stout and Griefel, the only difference lying in the fact that the magnet is rotated instead of the torsion head. The exciting coils of the electromagnet are energised and if the crystal is not at the zero position a deflection of the suspension system is observed. The magnet is rotated until there is no deflection on make and break of the current. This gives the 'zero position' of the balance and the corresponding position of the magnet is noted. From this position the magnet is rotated through any angle. This angle of rotation should be less than 45° and preferably greater than 30°. When the magnetic field is switched on the crystal will experience a couple and will try to align in the direction of the magnetic field. The crystal is restored to its original position by passing a current through the balancing coil. In order that the deflection from the 'zero-position' be less both the currents viz. the current through the electromagnet and that through the balancing coil should be increased or decreased simultaneously. Because the upper permanent magnet is placed high above the lower electromagnet and has no interaction with it, the torque acting on the coil is directly proportional to the current in it. This current is determined by measuring the potential drop across

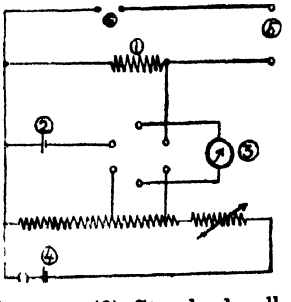

Figure 2—(1) Standard resistance. (2) Standard cell. (3) Multiflex Galvanometer. (4) Driving cell. (5) To current regulated power supply. (6) Magnet.

a standard resistance with the help of a precision potentiometer capable of measuring upto microvolt.

For calibrating the balance the current I_s required for balancing the couple due to a standard specimen is found out in the abovementioned way. For measuring anisotropy of any substance the standard sample is replaced by it and the coil brought to the original position by rotating the torsion head, if required. We have seen during measurement that if the hook-joint is made rigid by a drop of wax and opened by melting the wax in the joint with a hot brass rod carefully, the position of the coil is not at all altered on changing the crystal. Now, the current I_u required for balancing the couple for the unknown specimen is determined.

The couple experienced by the standard sample

$$\Gamma_s \propto I_s = \frac{A(\Delta\chi)_s m_s}{M_s} \sin 2\theta. \quad \ldots (1)$$

and that by the test sample

$$\Gamma_u \propto I_u = \frac{A(\Delta\chi)_u m_u}{M_u} \sin 2\theta \quad \ldots (2)$$

where A is the constant of proportionality and $\Delta\chi$, m, M correspond to magnetic anisotropy, mass and molecular weight of the crystal. θ denotes the angle through which the magnet has been rotated in both cases. The subscripts s and u stand respectively for the standard and test sample.

If the angle of rotation θ is the same for both the cases then

$$\Delta\chi_u = \Delta\chi_s \frac{I_u}{I_s} \cdot \frac{m_s}{m_u} \cdot \frac{M_u}{M_s} \quad \ldots (3)$$

RESULTS

The performance of the balance was examined by measuring the current required to balance the couple acting on the crystal for different angular positions of the crystal with respect to the field direction. According to the relation (1) or (2) the ratio of sine 2θ and that of the couple should be constant. We measured the couples acting on the $CuSO_4$, $5H_2O$ crystal by rotating the magnet through 30°, 35°, 40° and 44° from its zero position and the linearity is observed to be within 0.05% which demonstrates the excellent response of the balance. The graph in fig. 3 shows the linearity between sin 2θ's and the corresponding balancing e.m.f.'s as the measure of the couples. It may be pointed out here that this check should be taken as the true test of the reproducibility of the balance itself since in these measurements only the couple acting on the crystal is changed by rotating the magnet keeping all other factors constant. However, the overall accuracy in

measurement of anisotropy depends on various factors, e.g., perfection of the crystal, the correct mode of suspension of the crystal and the homogeneity of the magnetic field over the region. The reproducibility and accuracy of our balance is also checked by measuring the balancing currents for crystals of different masses

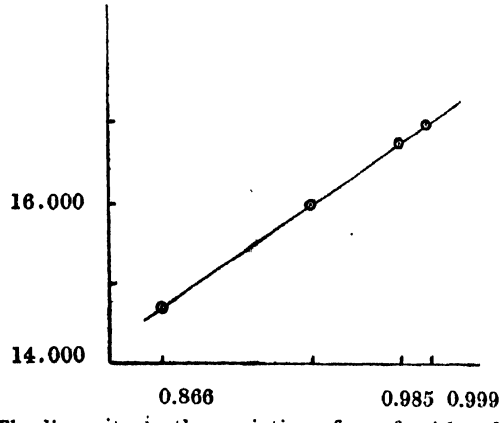

FIG. 3—The linearity in the variation of e.m.f. with values of sin 2θ.
Abscissae—Values of sin 2. Ordinate—e.m.f. in μV.

of the specimen in the same magnetic field. It is evident from the expression of the anisotropy that the variation of e.m.f. with mass should be linear. Using different crystals of $CuSO_4$, $5H_2O$ we find that the linearity is within 0.2%. The higher error in this case is obviously more due to lack of perfection in the crystals and mode of suspension and inhomogeneity of the fields rather than the reproducibility of balance. A graph between different masses of $CuSO_4$, $5H_2O$ crystal with the corresponding e.m.f.'s is shown in fig. 4.

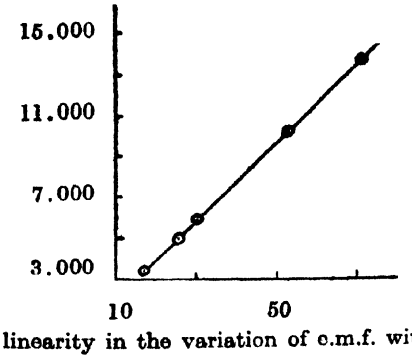

FIG. (4)—The linearity in the variation of e.m.f. with mass of the crystal.
Abscissae—Mass in mg. Ordinate—e.m.f. in μV.

The magnetic anisotropy of three different crystals belonging to the monoclinic system were measured with the balance. For this purpose the field was calibrated first with $CuSO_4$, $5H_2O$ crystal (with c-axis vertical). Measurement

was done by suspending the sample with *b*-axis vertical. The results are given in table 1. The overall accuracy of these values was estimated as less than 0.5%.

As is obvious from the description and operation of the balance it is extremely simple in construction and easy to operate. The changing of samples is also effected very quickly. If the phototube null detecting system is made enough sensitive the same balance is capable of giving highly accurate values both for

TABLE 1

Crystal	$(\chi_1-\chi_2)\times 10^6$		Temperature
	Present value	Previous workers' value	
$CuK_2(SO_4)_2$	327.7	322.3*	
$NiK_2(SO_4)_2$	133.8	131.2*	300°K
$CoK_2(SO_4)_2$	2530	2540**	

* Dutta (1954).

** Guha Thakurta *et al* (1966).

DISCUSSION

crystals of low and high anisotropy since it only involves measurement of e.m.f. which can be done pretty accurately by a good potentiometer with a sensitive galvanometer.

A few points of caution may, however, be mentioned at this point. During the course of measurement it was discovered that the error due to the anisotropy of the pyrex suspension rod which lies between the pole gap may cause appreciable error. Hence it is absolutely necessary to use as thin rod as possible and check each of them before use. Another factor which needs special attention for ensuring satisfactory working of the balance is the elimination of zero shift. Various factors are responsible for such shift in these sensitive instruments. If, however, particular care is bestowed on the neatness in constructing the balance this can be reduced to negligible proportions. The suspension fibre and phosphorbronze spirals should be scrupulously cleaned; the soldered joints should be as neat as possible and one should avoid any sharp bend in the bronze spirals : finally one should avoid any drastic temperature change during the course of the experiment as far as possible.

The distance between the coil and the electromagnet should be made large enough to avoid any appreciable stray field at the position of the coil compared to the field due to the local magnet. This is necessary since the angular position of the magnet has to be changed in course of measurement and this would entail a corresponding change in the effective field on the coil. The comparative strength

of the stray field could be detected by keeping a small current running through the coil and noting whether there is any change in the deflected position of the mirror by rotating the electromagnet.

The figures 3 and 4 display the fine performance of the balance. High linearity of e.m.f with the mass and sin 2θ shows the high reproducibility of the instrument. The UNICO electromagnet, probably the only Indian product in this category, was used in the measurement. It was found tht the homogeneity of the field with a pole gap of 4 cm was restricted within 1.2 cm around the centre of the pole gap.

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