

MAGNETOSTRICTION IN SINGLE CRYSTALS OF PURE BISMUTH
AND THE EFFECT OF ADDED IMPURITIES

Thesis by
Alexander Wolf

In Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
California Institute of Technology
Pasadena, California

1932

TABLE OF CONTENTS

	<u>Page</u>
LIST OF PRINCIPAL SYMBOLS	III
INTRODUCTION	1
STATEMENT OF PROBLEM	3
THE THEORY OF MAGNETOSTRICTION	4
METHODS OF MEASURING MAGNETOSTRICTION	8
THE METHOD OF THIS INVESTIGATION	10
DESCRIPTION OF APPARATUS	13
DESCRIPTION OF CRYSTALS	21
TECHNIQUE OF THE EXPERIMENT	23
(A) Production of crystals	23
(B) Calibration of apparatus	24
(C) Magnetostriction test	30
DISCUSSION OF CORRECTIONS AND ERRORS	34
(A) Imperfections in crystals	34
(B) Errors in calibration	36
(C) Errors in magnetostriction measurement	37
(1) Stray effects	37
(2) Magnetostriction of frame	39
(3) Mechanical stress in crystal	39
(4) Effect of inhomogeneity of field	40
(5) Thermal effects	42
(D) Summary	46

MAGNETOSTRICTION IN SINGLE CRYSTALS OF PURE BISMUTH	47
THE EFFECT OF IMPURITIES ON MAGNETOSTRICTION IN BISMUTH	52
MODULUS OF MAGNETOSTRICTION IN THE LIGHT OF THE THERMODYNAMIC THEORY	56
CONCLUSION	57
SUMMARY	58
REFERENCES	60

LIST OF PRINCIPAL SYMBOLS

- P-3 - - - - pertaining to the orientation of a long cylindrical crystal, indicates that the trigonal axis of the crystal is parallel to the axis of the cylinder
- P-1, 0° - - pertaining to the orientation of a long cylindrical crystal, indicates that the trigonal axis is at right angles to the axis of the cylinder, and one of the binary axes is parallel to the axis of the cylinder
- P-1, 30° - - same as above, except that one of the binary axes is inclined at 30° to the axis of the cylinder
- m - - - - modulus of magnetostriction. It is defined by the relation $\Delta L/L = \frac{1}{2} m H^2$, where $\Delta L/L$ is the magnetostriction, and H is the magnetic intensity

INTRODUCTION.

The term magnetostriction is commonly used to designate all the phenomena of strain or stress which occur in certain substances when the latter are placed in a magnetic field. This paper, however, is confined to the measurement and discussion of only one of these phenomena, viz., the so-called Joule Effect. This is a change in the length of a long rod when subjected to the action of a homogeneous magnetic field, the direction of which coincides with the axis of the rod. The term magnetostriction, as used throughout this paper will designate the Joule Effect only, and will be expressed as a strain, i.e., as change in length per unit length of rod.

The effect was first measured by Joule¹⁾ in 1842 on a rod of iron. Later investigators extended Joule's work to cobalt and nickel, and their alloys, as well as to the other ferromagnetic alloys. As was only natural, even the earliest investigators in the field became interested in the question of magnetostriction in diamagnetic substances, and chose bismuth for their experiments, as the metal which shows diamagnetism to the most marked extent. Aubel²⁾ in his review of the literature up to 1903 on the subject of magnetostriction in bismuth quotes the work of Tyndall in 1870, Bidwell³⁾ in 1888 and 1899, Grimaldi¹⁸⁾ in 1889, Aubel¹⁹⁾ in 1892, Knott¹⁷⁾ in 1899, Wills⁴⁾ in 1902, and calls attention to the fact that all these experiments gave negative results. Negative results

were later obtained by Hobbie⁵⁾ in 1922 and Schulze⁶⁾ in 1928. Finally, in 1929 Kapitza⁷⁾ reported in a letter to Nature that he had found magnetostriction in single crystals of bismuth, that it is positive or negative, depending on the crystal orientation, its order of magnitude is 5×10^{-5} in a field of 300,000 gauss, and it varies approximately as the square of the field.

It became immediately apparent why the earlier investigations gave negative results. Under ordinary laboratory conditions it is difficult to obtain fields much in excess of 3000 gauss, except in narrow air-gaps between iron pole-pieces, which are not suitable for the measurement of magnetostriction. Now, in a field of 3,000 gauss the magnetostriction in a single crystal of bismuth would be of the order of 5×10^{-9} . Actually, all the earlier investigations were made on polycrystalline rods, in which the magnetostriction is about one fifth of that in crystals. Also, in his early report Kapitza overestimated the effect by a factor of almost two, so that the magnetostriction which actually occurred in the early experiments was less than 1×10^{-9} , which was well below the limits of sensitivity of all the apparatus used. The sole exception is the work of Hobbie⁵⁾, who claimed a sensitivity of 3×10^{-12} , but used a field of only 12 gauss, so that he also could not have found the effect.

Early in 1931 Dr. A. Goetz suggested to the writer that he attempt to measure magnetostriction in single crystals of pure bismuth, and bismuth containing small amounts of added impurities,

using for this purpose the 500 KW solenoid at the physical laboratory of the Mt. Wilson Observatory.

Subsequent to this, there appeared in 1931 a paper by Bryan and Heaps⁸⁾ again reporting negative results in their attempt to measure magnetostriction in single crystals of bismuth.

Finally, in 1932, Kapitza⁹⁾ published a detailed account of successful measurements of magnetostriction in crystals of pure bismuth.

STATEMENT OF PROBLEM

The purpose of this investigation was two-fold, viz.:

1) to check as far as possible the work of Kapitza on pure bismuth crystals and 2) to determine the effect of the addition of impurities on the magnetostriction in bismuth crystals.

The reasons for checking the work of Kapitza are again two-fold, viz.:

A) Kapitza's measurements are taken in a transient field lasting only two-hundredth of a second between the instant when the field starts building up, and the time when the field has decayed completely. It was thought that the crystal may take some time to adjust itself to the magnetic field, and that this time may be appreciable compared with one-hundredth of a second. Hence it would be desirable to determine whether measurements in a steady field, as obtainable in the Mt. Wilson solenoid, would not give results materially different from those taken in a transient field.

B) Kapitza's apparatus is designed for the measurement of the

large strains occurring in fields up to 300,000 gauss, and, hence, is not sensitive enough in the range covered by the Mt. Wilson solenoid, viz. up to 25,000 gauss. Measurements taken in the very strong fields used by Kapitza are also somewhat questionable, unless checked in moderate fields, for the reason that the strains produced in the crystals are so great that they may actually exceed the elastic limit of the material. This was actually observed by Kapitza in the case of crystals which were grown with their principal crystallographic axis inclined at about 45 degrees to the axis of the rod.

As far as the second, and main part of the investigation is concerned, the determination of the effect of impurities on the magnetostriction of single crystals of bismuth is a logical continuation of the general program of investigations conducted under Professor Goetz by Hergenrother²¹⁾, Focke²²⁾, and Hasler²³⁾ on the effect of small amounts of impurities on the various physical properties of bismuth single crystals. It appears that the study of the effect of impurities is a powerful tool in the field of crystal physics. It is hoped that this work will eventually throw a light on the structure of a real crystal and on the nature of crystal diamagnetism, both problems being unsolved at this writing.

THE THEORY OF MAGNETOSTRICTION

A satisfactory theory of magnetostriction in a crystal should deduce the effect of the magnetic field on interatomic bonds, and hence on the configuration of the crystal. Such a theory does

not exist, possibly because the nature of the interatomic bonds is not well understood.

With the exception of the most modern theories, applicable only to ferromagnetic materials, and based on quantum-theoretical considerations, all the theories of magnetostriction deal with the subject from the point of view of the first law of thermodynamics. The theories succeed in deriving a relation between magnetostriction and the statistical elastic and magnetic properties of a body, but do not give any idea as to the mechanism of the phenomenon. This, of course, is not to be expected from a thermodynamical treatment.

The best method to be followed appears to be that of variations. We consider a long diamagnetic rod of length L and sectional area A , with its axis along the magnetic lines of a homogeneous field. The length, L , of the rod is supposed to be large compared with the diameter. The distortion of the field produced by the rod is disregarded. The magnetic energy per unit volume is E in the rod, and E_1 in the air, where

$$E = \frac{1}{4\pi} \int \mu H dH, \quad E_1 = \frac{H^2}{8\pi} = \frac{1}{4\pi} \int H dH$$

If $V = A L$ is the volume of the rod, and V_1 is the volume of air in some arbitrary surface enclosing the rod, but so described that it does not come near the rod at any point, then the total magnetic energy inside the surface is

$$E_m = V E + V_1 E_1$$

If the rod is now subjected to a virtual elongation δL , the change

in the magnetic energy is

$$(1) \quad E_m = \frac{\partial E_m}{\partial L} \delta L = \left(\frac{\partial V}{\partial L} E_1 + \frac{\partial V_1}{\partial L} E_1 + V \frac{\partial E}{\partial L} + V_1 \frac{\partial E_1}{\partial L} \right) \delta L$$

$$\text{We note that } \frac{\partial V}{\partial L} = -\frac{\partial V_1}{\partial L} = A(1 - 2\sigma)$$

where σ is Poisson's ratio. Also

$$\frac{\partial E}{\partial L} = \frac{1}{4\pi} \int \frac{\partial \mu}{\partial L} H \, dH$$

If p = longitudinal stress in the rod

Y = Young's modulus,

$$\text{then } \frac{1}{L} \frac{\partial L}{\partial p} = \frac{1}{Y}, \text{ and}$$

$$\frac{\partial \mu}{\partial L} = \frac{Y}{L} \frac{\partial \mu}{\partial p}$$

Hence

$$\frac{\partial E}{\partial L} = \frac{1}{4\pi L} \int Y \frac{\partial \mu}{\partial p} H \, dH$$

$$\text{and } \frac{\partial E_1}{\partial L} = 0$$

Substituting in (1):

$$E_m = A(1 - 2\sigma) \delta L \left\{ \frac{1}{4\pi} \int \mu H \, dH - \frac{1}{4\pi} \int H \, dH \right\} + \frac{A \delta L}{4\pi} \int Y \frac{\partial \mu}{\partial p} H \, dH$$

Putting $\mu = 1 + 4\pi x$, where x is the susceptibility

$$\delta E_m = A \delta L \int \left\{ x(1 - 2\sigma) + Y \frac{\partial x}{\partial p} \right\} H \, dH$$

The change in elastic energy produced by the variation δL is

$$E_e = p A \delta L$$

Since the system is in equilibrium, the first-order variation in

the potential energy is zero. Hence

$$\delta E_m + \delta E_e = 0$$

Substituting the values obtained above, we obtain

$$p = - \int \left\{ Y \frac{\partial x}{\partial p} + x(1 - 2\sigma) \right\} H dH$$

Since $p = Y \Delta L/L$

$$\frac{\Delta L}{L} = - \frac{1}{Y} \int \left\{ Y \frac{\partial x}{\partial p} + x(1 - 2\sigma) \right\} H dH$$

If Y is independent of H

$$\frac{\Delta L}{L} = - \int \left\{ \frac{\partial x}{\partial p} + \frac{x}{Y}(1 - 2\sigma) \right\} H dH$$

The identical result is obtained by Ieduc¹⁶⁾ by a somewhat different reasoning.

In the case of bismuth at room temperature the susceptibility, x , is independent of H . Hence $\partial x / \partial p$ is independent of H , so that the integration can be performed. The formula reduces to

$$\frac{\Delta L}{L} = - \frac{H^2}{2} \left\{ \frac{\partial x}{\partial p} + \frac{x}{Y}(1 - 2\sigma) \right\}$$

$\Delta L/L$ is the longitudinal magnetostriction, expressed as a strain, and is proportional to the square of the field. The term in the parenthesis can be used conveniently to describe magnetostriction, since the field then does not have to be specified. We shall designate this term by "m", and shall call it the "modulus of magnetostriction". By definition, then, the experimental value of m is

$$m = 2 \Delta L / H^2 L$$

We shall now show that, in the case of bismuth, the second term in the theoretical expression for m is negligible compared with the first. The maximum value of x/Y is obtained when the magnetic intensity is parallel to the principal axis of the crystal. Then, at room temperature,

$$x = -1.04 \times 10^{-6} \times 9.8 \quad 10)$$

$$1/Y = 1.62 \times 10^{-12} \quad 11)$$

The approximate value of σ is $1/4$. A simple calculation shows that the second term in the expression for m is about 8×10^{-18} . Since the experimental value of m is about 6×10^{-16} , the term just calculated can be neglected, and we can write the equation for magnetostriction as

$$\frac{\Delta L}{L} = - \frac{H^2}{2} \frac{\partial x}{\partial p}$$

It should be remembered that this is based on the assumption that Y is not a function of H . There is no experimental justification for the latter assumption. Moreover, in view of the fact that the elastic forces are of electrical nature, it is very likely that Y does vary with H . Hence, it would not be surprising if experiments on magnetostriction in bismuth did not confirm the variation of $\Delta L/L$ with the second power of H .

METHODS OF MEASURING MAGNETOSTRICTION

All methods of measuring magnetostriction involve the

construction of some form of extensometer which will magnify the small changes in length which are to be measured. The extensometers described in the literature fall into four general classes, viz.:

- (A) mechanical
- (B) optical
- (C) electrical
- (D) special methods

(A) Mechanical Extensometers. This is the earliest type, since it was used by Joule¹⁾ in his original investigations on magnetostriction. It is also the type which was employed most widely. It consists of some combination of mechanical levers with an optical lever. Theoretically this method will yield any magnification desired. The practical difficulties lie in the elimination of lost motion, prevention of vibrations, and prevention of spurious deflections caused by thermal expansion of the mechanical system.

(B) Optical Methods. These methods employ some form of interferometer. The great advantage of the method lies in the fact that the calibration of the apparatus is extremely simple. It would be difficult to make this method sufficiently sensitive for the measurement of magnetostriction in bismuth, as can be seen from the fact that the total strain in this experiment is only about 2.5×10^{-7} . With a sample 10 cm long the total change in length is then only 2.5×10^{-6} cm, which is equivalent to a shift

of one-tenth of a fringe. The shift of one-tenth of a fringe would then have to be measured with an accuracy depending on the accuracy desired in the final result.

(C) Electrical Methods. These consist of some modification of the Whiddington ultramicroscope. The sensitivity attainable is very high, but the measurements take a fairly long time, since a large number of beats must be counted in order to obtain accuracy. Where the sample tested for magnetostriction is undergoing a continuous thermal expansion, which is comparable in magnitude with the magnetostriction, the ultramicroscope method appears to be at a disadvantage.

(D) Special Methods. McKeehan¹²⁾ at the Bell Telephone Laboratory devised a very ingenious method consisting of a simple optical lever, which converts the extension of the rod tested into the motion of a spot of light, and a photo-electric cell with which the position of the spot of light can be measured accurately. This method appears to be superior to all the preceding, since the mechanical system is very simple, the attainable sensitivity is high, and the speed with which readings can be taken depends only on the period of the galvanometer attached to the photo-electric cell.

THE METHOD OF THIS INVESTIGATION.

The measurement of magnetostriction in bismuth presents difficulties far exceeding those encountered in the case of ferromagnetic substances, because the effect under investigation is of an

entirely different order of magnitude. Whereas in the ordinary laboratory solenoid, producing a field of about 3,000 gauss, the magnetostriction in a ferro-magnetic substance is usually several times 10^{-5} , the bismuth crystal under the same circumstances will show an effect of about 3×10^{-9} . This much was known from the preliminary report of Kapitza⁷⁾. Even in the 500 KW solenoid of the Mt. Wilson Laboratory the magnetostriction in bismuth is still only about 2.5×10^{-7} . Thus, by resorting to the large solenoid, the magnetostriction could be increased almost one-hundred times, but it was still only about one-hundredth of that shown by a ferro-magnetic material in a moderate field. It must also be realized that an increase in the magnetic field intensity does not make the measurement as much easier as a simple comparison of the figures might indicate, for, at the same time, the disturbance on the apparatus, produced by the magnetic field, is increased to a marked extent, be it through heating, transient currents induced by the field, vibration of the necessary rotating machinery, etc. Thus the development of proper apparatus is much more difficult than in the case of experiments on ferro-magnetic substances.

The method adopted in this investigation presents certain similarities to that of McKeehan¹²⁾, described in the last paragraph of the preceding section. The change in length of the crystal is converted into the rotation of a small mirror by a very simple mechanical arrangement, in which little attempt is made at magnification. A beam of light coming from a fixed slit is reflected by

the mirror onto a Moll Thermo-Relay manufactured by the firm of Kipp and Zonen. This is an instrument which was designed for the purpose of magnifying the deflection of a galvanometer. It consists of a differential thermo-couple mounted in a vacuum, with the junctions at a distance of about 1 cm from each other. When a spot of light falls on the point exactly half-way between the junctions, both junctions are heated uniformly, and no current flows in the external circuit. When the spot of light is moved toward one or the other of the junctions that junction is heated more than the other, and a current flows in the external circuit. This current is measured with a galvanometer. The instrument has a linear calibration over such a wide range that in practice it is not necessary to start with the spot of light exactly half-way between the thermo-couple junctions. The sensitivity of the device depends, of course, on the intensity of the spot of light, and on the sensitivity of the galvanometer. As used in this experiment a galvanometer deflection of 1 mm corresponded to a motion of the spot of light of about 0.0007 mm, a magnification of about 1400 times. The great advantage of the instrument lies in the fact that the spot of light need not be sharp. In this experiment the spot was from two to three millimeters in diameter. This width is actually necessary, since the sensitivity depends on the total energy of the light falling on the device.

The magnification obtained in the optical lever, which converts the change in length of the crystal into a motion of the spot

of light, was about 300 times. Hence the total magnification was about 400,000 times, i.e., a deflection of 1 mm on the galvanometer scale corresponded to a change in length of the crystal of 2.5×10^{-6} mm. Since the crystals used were about 100 mm long, one millimeter on the galvanometer scale corresponded to a strain of one part in forty-million.

This method offers the same advantage as that of McKeehan's which was described above, since the sensitivity is high, readings can be taken quickly, and the absence of mechanical magnifying levers makes the apparatus comparatively insensitive to external vibrations. This last feature is of extreme importance in the present instance, since the solenoid was supplied with direct-current from a 600 KW motor-generator set located in the same room and producing a great deal of vibration.

DESCRIPTION OF APPARATUS.

The essential part of the apparatus is the frame-work in which the crystal is mounted, and the arrangement whereby the change in length of the crystal is transformed into the rotation of a mirror. This part of the apparatus, in its proper place in the solenoid, is shown in Fig. 1.

A brass block (1) is held rigidly in the wooden piece (2), which in turn is bolted to an outside wooden frame-work, not shown in Fig. 1. Two fused quartz tubes (3) are cemented in the brass block. Aluminum discs (4 to 10) are cemented on the quartz tubes, forming a rigid frame. The disc designated (9) holds a copper

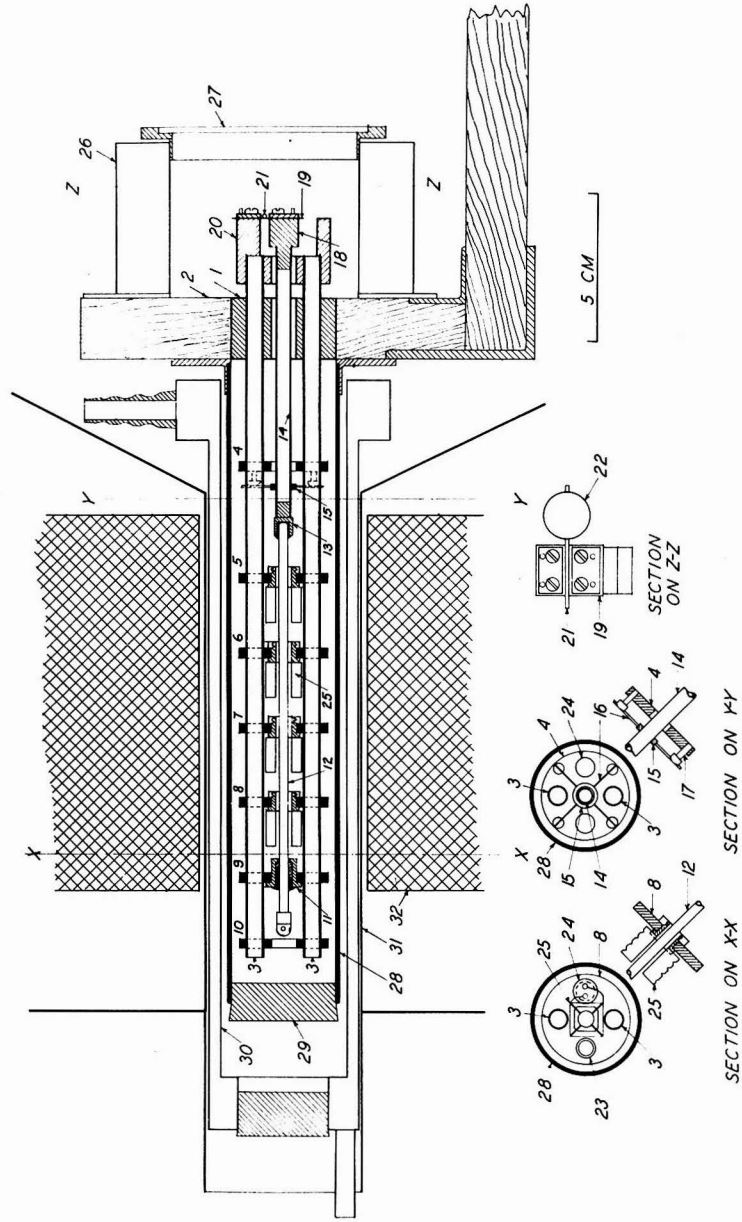


Fig. 1.

cup (11) in which one end of the crystal tested (12) is fixed with Wood's Metal. The other end of the crystal is fixed similarly in a copper cup (13), cemented in turn to the fused quartz tube (14), which extends to the right, passing freely through the brass block (1). The left end of tube (14) is held in a brass ring (15), which has soldered to it radially four thin bronze wires (16), which in turn are soldered to the heads of four pins (17) screwed into the aluminum disc (4). This feature of the apparatus is best seen in the section in the lower center of Fig.1. It is seen that the left end of tube (14) is free to move through small distances to the right or left. The right end of this tube carries a small brass block (18). To the right face of this block is clamped a very thin bronze strip (19). The upper end of this strip is clamped to the face of a brass block (20), cemented onto the quartz tubes (3) which form the main frame-work. The vertical clearance between (18) and (20), which is also the free length of the bronze strip (19) is 3 mm. Along the center of the free part of the bronze strip (19) is soldered a copper wire (21), which carries a 5/8-inch galvanometer mirror (22). This part of the apparatus is shown best in the section in the lower right of Fig.1.

It is seen that the central quartz tube (14) is constrained to a small horizontal motion, which, however, is amply sufficient to permit the crystal under test to expand and contract freely. This matter will be discussed more fully later. It can be readily seen that a change in the length of the crystal results in a hori-

zontal motion of the brass block (18) relative to (20), and that the bronze strip transforms this motion into the rotation of the mirror (22) around a horizontal axis. The movement is entirely free from friction and there is no possibility of lost motion.

For purposes of calibration it was necessary to be able to raise the temperature of the crystal by about 0.2 deg.C. This could be accomplished by means of a heating coil made of tungsten wire wound on a thin glass tube. This coil (23) was as long as the crystal, and was placed along the crystal, running through holes in the aluminum discs. Holes (24) on the opposite side of the crystal hold insulating bushings, which carry the leads of a platinum resistance thermometer wound concentrically with the crystal on four mica frames (25), attached to the aluminum discs (5,6,7,8). A section showing the mica frames can be seen on the lower left of Fig. 1. The platinum thermometer is spread out over the full length of the crystal, so as to obtain an average of temperature, in case of a temperature gradient. The thermometer also is needed for purposes of calibration, which will be discussed later. The wire used in the thermometer is 0.05 mm in diameter and about one meter long; its resistance is 60 ohm at 25 deg.C, and changes by 0.196 ohm for each degree centigrade.

The apparatus described above forms a distinct unit, which does not come in direct contact with the solenoid. It is protected on the right by a water-jacket (26) with a glass window (27) in front of the moving mirror. On the left the apparatus is covered

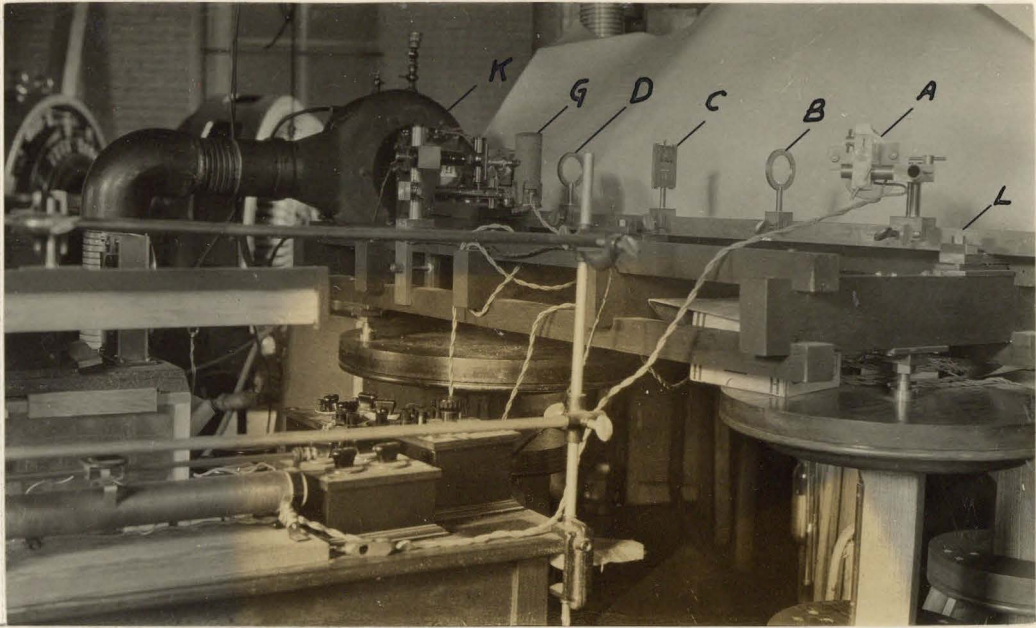


Fig. 2.

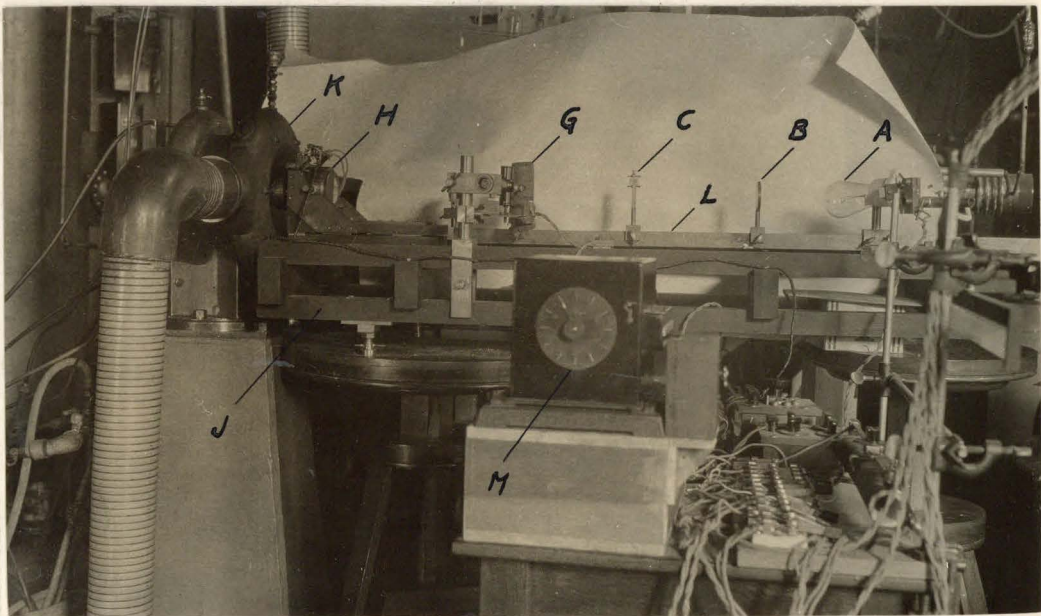


Fig. 3.

by a glass tube (28) closed with a cork (29). Between the above unit and the solenoid is interposed a water-jacket (30), intended to maintain the crystal at a uniform temperature. The outer shell of the solenoid (31), and the position of the coils (32), are indicated in the figure.

The complete assembly of the apparatus is best seen in the photographs (Figs. 2 and 3) and a diagram of the optical system is shown in Fig. 4. The external part of the unit described above is shown at (H) in Fig. 3. The unit is bolted to a stiff wooden framework (J), which holds also a brass optical bench (L). The optical bench carries a series-street-lighting lamp (A), which is the source of energy for operating the thermo-relay (G). The optical system consists of a horizontal slit (C), two convex lenses (B,D), and a cylindrical lens (F), shown in Fig. 4, but not on the photographs. This lens is placed just in front of the thermo-relay (G). Its axis is vertical, so that it increases the intensity of the light falling on the thermo-relay, without changing the length of the optical arm.

The current in the thermo-relay circuit is measured with a Leeds and Northrup high-sensitivity galvanometer, critically damped, and not shown in the figures. The galvanometer has a period of 15 sec., a resistance of 500 ohms, and a critical damping resistance of 6000 ohms. The deflection of the galvanometer is recorded on a moving strip of photographic paper, driven by clock-work (M). A timing device makes a mark on the paper at intervals of 15 seconds.

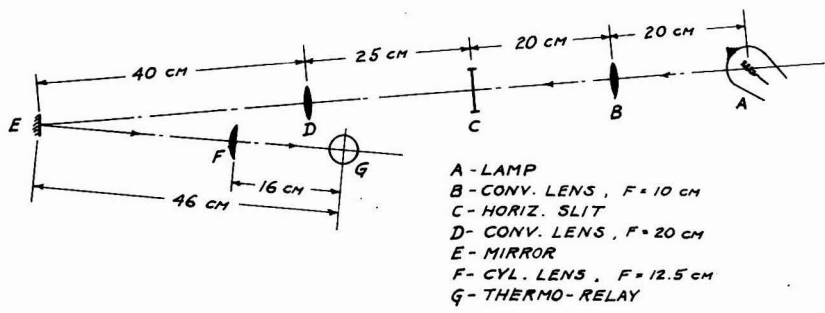


Fig. 4.

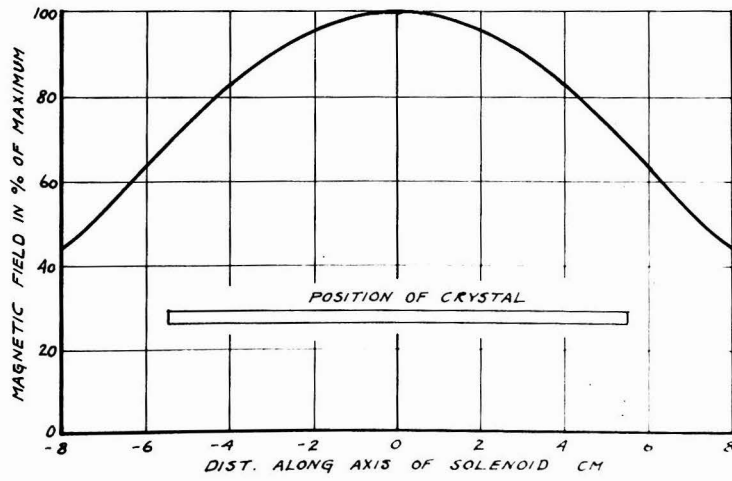


Fig. 5.

Magnetic field of the solenoid

The solenoid is shown at (K) in Fig. 2 and 3. It consists of two coils, one inside the other, connected in parallel. Both coils have approximately the same resistance, so that the total current is split almost evenly between the coils. The specifications of the solenoid are as follows:

Inner diam. of winding	2-3/8 in.
Outer " " "	8-5/16 in.
Length of winding	5 in.
No. of turns in inner coil	126
" " " " outer "	84
Conductor - copper tape	3/8 x 1/16 in.
Max. current - both coils	4000 amp.
" voltage	125 volt
" power - both coils	500 KW

The coils of the solenoid are enclosed in a brass shell, having a central opening 2 inches in diameter. Cooling is effected by means of transformer oil pumped through the coils and through a system of pipes immersed in a large water tank. The power is supplied by a 600 KW motor-generator set, which can be seen in the left background of Fig. 2.

The calibration of the solenoid was carried out with a Grassot Fluxmeter, made by the Cambridge Scientific Instrument Co. The field at the centre of the solenoid was 28,300 gauss with 4,000 amps. The field decreased symmetrically on both sides, as shown in Fig. 5. The root-mean-square field averaged over a cen-

trally placed crystal, 11 cm long, was 91% of the field at the centre, i.e., 25,750 gauss with 4,000 amps.

In the course of the work parts of the solenoid became gradually short-circuited, so that the field for a given current became less. Since it was not safe to increase the current beyond 4,000 amps, the measurements had to be carried out in a weaker field. The final field at the center of the solenoid was 23,400 gauss with 4,000 amps, and the r.m.s. field over 11 cm was 20,400 gauss.

DESCRIPTION OF CRYSTALS

The crystals used in this investigation were grown in the shape of rods 2 to 3 mm in diameter and at least 12 cm long. Two principal orientations were studied. The crystals designated as P-1 had the principal (trigonal) axis at right angles to the axis to the rod. Hence the axis of the rod was in the principal cleavage plane, and magnetostriction was measured at right angles to the principal axis. These crystals fall into two groups, viz.:

- 1) one of the binary axes along the axis of the rod
- 2) one of the binary axes inclined at 30 deg. to the axis of the rod.

The first group is designated as P-1, 0° , the second as P-1, 30° . Only one crystal of the latter group was tested.

The second class of crystals, designated as P-3, had the principal (trigonal) axis along the axis of the rod, and the principal cleavage plane at right angles to the axis of the rod.

Hence magnetostriction was measured parallel to the principal axis. This last orientation is more difficult to produce. The actual crystals had the principal axis inclined at about 4 deg. to the axis of the rod.

The bismuth used was of "commercial" grade, obtained from the Merck Chemical Company. Two separate lots were used, designated here as Bismuth H, and Bismuth J. These lots were not analysed for impurities. It was found, however, that the magnetic anisotropy of crystals grown from Bismuth H and J was the same as that for crystals grown from lots designated as H and F, which were obtained previously from the same source. Since the magnetic anisotropy of bismuth crystals is very sensitive to impurities, there is every reason to believe that lots H and J are substantially as pure as lots E and F. A spectroscopic analysis of the latter, made by Mr. Hasler, gave the following results:

Bismuth	No. of foreign atoms per 100 atoms of bismuth (atomic percentage)	
	E	F
Copper	0.007	0.001
Silver	0.013	0.006
Tellurium	0.000	0.000
Thallium	0.000	0.000
Lead	0.014	0.002
Total	0.034	0.009

The reason for using the Merck "commercial" bismuth is

that it was found to be purer than "chemically pure" and "electrolytic" bismuth obtained from other sources.

TECHNIQUE OF THE EXPERIMENT

The experimental procedure is divided into three steps, viz.:

- (A) Production of crystals
- (B) Calibration of apparatus
- (C) Magnetostriction test

(A) Production of crystals.

The crystals were grown by the method developed by Goetz¹³⁾ following exactly the somewhat simplified procedure described in detail by Focke¹⁰⁾. There is no need to repeat the description in this place.

The P-1 crystals were grown at the rate of about 6 mm per minute. This is fast enough to prevent the accumulation of impurities at one of the ends.

A great deal of difficulty was experienced in growing the P-3 crystals. This was finally solved by growing them at the rate of only 1 mm per minute, or slightly less. In the case of crystals with added impurity this leads, according to Focke, to an accumulation of the impurity at one of the ends. No tests were made on this effect. It is believed, however, that the irregularity in the magnetostriction results on P-3 crystals containing lead, may be caused by this factor. Nevertheless, the effect of impurities on

the magnetostriction in the P-3 crystals is not so great that serious errors could arise from the above cause. The question of the distribution of impurities is discussed at greater length later.

(B) Calibration of apparatus.

The calibration of the apparatus cannot be calculated accurately from its dimensions, because of the manner in which the change in length of the crystal is transformed into the rotation of a mirror. An experimental determination is required. The manner in which this is accomplished is as follows:

The crystal to be tested for magnetostriction is mounted in the apparatus and everything is put in its final test position. The position of the thermo-relay is adjusted so that the reading of the galvanometer connected to it is near zero. The temperature of the crystal is then changed by about 0.2 deg.C, and the corresponding deflection of the thermo-relay galvanometer is noted. Now, if

A - - - coeff. of thermal expansion of crystal

A_1 - - - " " " " " the frame in which
crystal is mounted

ΔT - - change in temperature

S - - - sensitivity, expressed as strain ($\frac{\Delta L}{L}$) per unit
deflection of galvanometer, D .

L - - - length of the crystal

then

$$\frac{\Delta L}{L} = A \Delta T$$

also
$$\frac{\Delta L}{L} = S D$$

Hence
$$S = \frac{A \Delta T}{D}$$

The above would be true if the frame holding the crystal had a zero coefficient of thermal expansion. Actually it has a coefficient (A_1) different from zero, though small. This necessitates a correction in S , viz.:

$$S = \frac{(A - A_1) \cdot \Delta T}{D}$$

The sensitivity, S , depends on the intensity of the spot of light falling on the thermo-relay. Now, in practice, the calibration was performed with the thermo-relay lamp connected to the lighting circuit, whereas during the magnetostriction test the lamp was operated by a battery. Hence it was desirable to obtain a quantity expressing the sensitivity without reference to the intensity of the light. To do this we must determine the intensity of the beam of light. By means of a micrometer screw we now displace the thermo-relay vertically through unit distance, and note the deflection of the galvanometer, say D_1 . We call D_1 the calibration of the lamp. It was found convenient to use as unit displacement of the thermo-relay a distance of $1/36$ mm, corresponding to ten degrees on the micrometer screw.

We now define a "sensitivity factor" F by the relation

$$F = S D_1 = \frac{D_1}{D} (A - A_1) \Delta T$$

If the lamp calibration during the magnetostriction test is found to be D_2 , the actual sensitivity is

$$S_1 = F/D_2 = S D_1/D_2$$

The sensitivity factor, F , would be a constant of the apparatus, determinable once for all, if it were not for the fact that the mechanical magnification is very sensitive to the exact shape assumed by the bronze strip (19, Fig. 1) which converts the change in length of the crystal into the rotation of the mirror (22, Fig. 1). The shape of this strip depends on the relative position of the two brass blocks to which the strip is clamped, and therefore changes slightly every time a new crystal is mounted. For this reason a separate calibration was conducted for each crystal, just before or after the magnetostriction test. The value of F for each crystal is given in the tables of results.

It still remains to describe the determination of the coefficients A , A_1 and ΔT in the expression for F .

The coefficients of thermal expansion of bismuth crystals, A , were taken from the yet unpublished work of Mr. T. L. Ho, at this Institute, who measured these factors for the two principal orientations of crystals containing various amounts of impurities. The values used can be found in the tables of results.

The coefficient of thermal expansion of the frame, A_1 , would be the coefficient for fused quartz (0.4×10^{-6} , Int. Crit. Tables,

vol. 4, p. 21), if it were not for the thermal expansion of the aluminum discs cemented to the quartz tubes and the copper cups in which the crystal is mounted. The effect of these metal parts was determined experimentally by mounting in the apparatus a fused quartz rod in place of the bismuth crystal, and conducting a regular calibration. In this case the thermal expansion is caused entirely by the above metal parts. Hence

$$F = \Delta T (A - A_1) D_1/D = \Delta T A_2 D_1/D$$

where A_2 is the required correction. Since A_2 is small it can be determined with sufficient accuracy by inserting in the formula an approximate value for F , and calculating A_2 . In this way the proper value of A_2 was found to be 0.2×10^{-6} . Hence

$$A_1 = 0.4 \times 10^{-6} + 0.2 \times 10^{-6} = 0.6 \times 10^{-6}$$

Since the thermal coefficient of expansion of bismuth crystals is about 12×10^{-6} and 16×10^{-6} for the two principal orientations, the correction A_1 is not very appreciable, so that it does not have to be known very accurately.

The determination of the last term in the sensitivity formula, ΔT , presents the greatest difficulty, since the platinum resistance thermometer measures the temperature of the air surrounding the crystal, rather than the temperature of the crystal. The obvious method would be to allow the crystal to come to a temperature equilibrium, then to change the amount of power supplied by the heat-

ing coil (23, Fig. 1), and again wait for temperature equilibrium. The time required for this was found to be of the order of one hour. In this time, however, the gradual distortions which go on in other parts of the apparatus introduce a drift in the readings of the thermo-relay galvanometer, so that a difference in its readings taken one hour apart, cannot be interpreted as due entirely to temperature expansion of the crystal. The remedy lies in shortening the time required for the calibration.

This was accomplished by changing the power supplied by the heating coil, back and forth at intervals of from 6 to 10 minutes. The resulting temperature variation of the air is somewhat as shown in Fig. 6, where curve A shows the air-temperature recorded against time. The temperature of the crystal, as reflected by the record of the thermo-relay galvanometer, is shown by curve B. Naturally the variation in the temperature of the crystal lags behind the variation of the air-temperature. The temperature of the crystal, however, is now known at any of the peaks, C_1 , C_2 , etc., since at the point where the temperature drift of the crystal changes sign, the crystal temperature must equal the air temperature. Hence the galvanometer deflection D corresponds to a change in temperature ΔT , as shown in the figure.

If a drift occurs owing to deformations of the apparatus, this can be recognized immediately, since in that case alternate peaks C_1 , C_3 , C_5 , etc. do not occur at the same temperature. A proper correction can then be applied, since the time-drifts, as

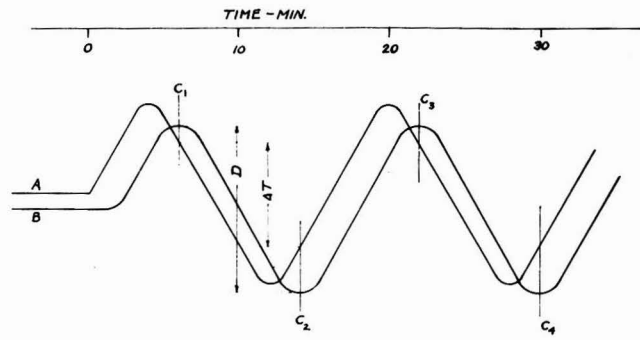


Fig. 6.

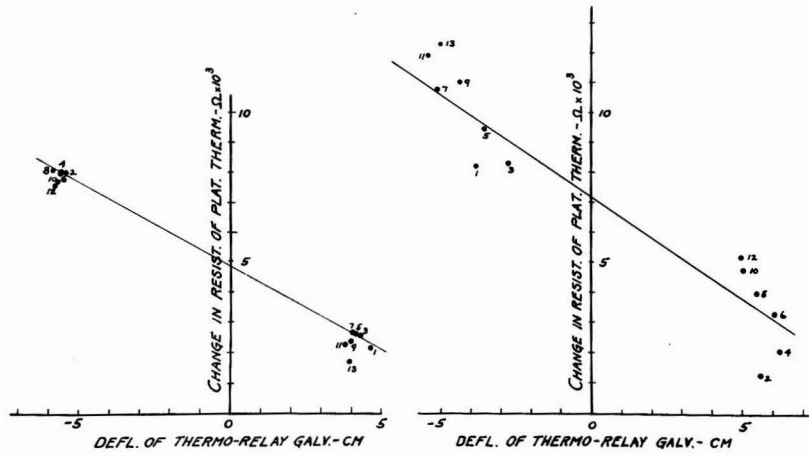


Fig. 7.

Fig. 8.

found, were always unidirectional, and their rate was practically constant for any given calibration. The great advantage of the method is found in its speed, which permits one to obtain a number of points on the calibration curve in such a short time that an external distortion-drift can be corrected for. In most calibrations about 12 points were used.

Typical graphs of thermo-relay galvanometer deflections (C_1 , C_2 , etc.) against the resistance of the platinum thermometer are shown in Figs. 7 and 8. Fig. 7 shows a case of no distortion-drift between points No. 1 and No. 8, and a small drift between points No. 8 and No. 13. Fig. 8 shows a rather extreme case of drift.

It should be noted that the method of calibration described above does not involve the measurement of the length of the crystal, which is one of the serious sources of error in most investigations of magnetostriction, particularly those made on short samples.

(C) Magnetostriction Test.

The magnetostriction tests were carried out on a time-schedule, with a timing device marking 15-second intervals on the records of the thermo-relay galvanometer, so that the points where the field was thrown on and off could be placed accurately on the records. Figs. 9, 10 and 11 show typical records of magnetostriction. The marks at the top indicate the 15-second intervals. The time-axis runs from left to right. The line in the centre is a record made by the thermo-relay galvanometer. Deflections downward

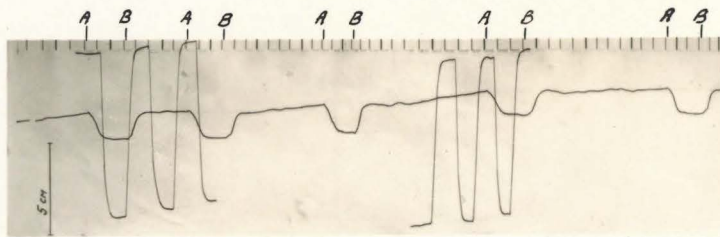


Fig. 9.

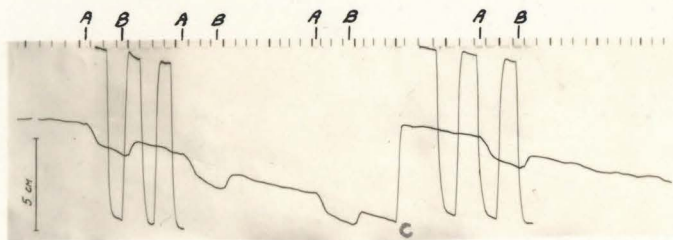


Fig. 10

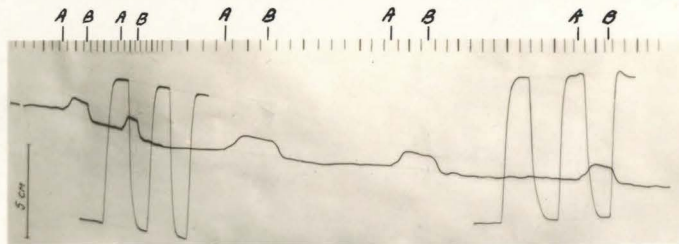


Fig. 11.

indicate an expansion of the crystal tested, deflections upward indicate contraction. Points A mark the time when the solenoid circuit was closed with a knife-switch on a current of about 2,000 amp. During the next 10 to 15 seconds the current was increased by means of a rheostat in the generator field to about 4,000 amp. The current was maintained at this strength for about 30 seconds. Points B indicate the time at which the breaking of the current was started, first with the field rheostat, and then with a series circuit-breaker. The time interval between points A and B was exactly 45 seconds. The above procedure was gone through four or five times for each crystal tested. The time between successive tests was governed by the heating of the solenoid.

The two sets of large deflections, extending almost across the records are the calibration of the lamp intensity, D_2 , required for the determination of the sensitivity. These were taken just before and just after each magnetostriction test. On the records shown in the figures the deflections were produced by a vertical back and forth displacement of the thermo-relay of $1/18$ mm (20 deg. of micrometer screw).

The magnetostriction in Fig. 9 is an expansion of 34×10^{-8} . This was the largest effect observed in any of the tests. Fig. 10 shows an expansion of 19×10^{-8} . Fig. 11 shows a contraction of 22.5×10^{-8} . A fairly rapid thermal expansion of the crystal can be seen in Fig. 10. In order that the line should not drift off the paper, the thermo-relay was displaced at the point marked C.

Immediately after each test of the type described above a mirror was attached with wax to the face of the glass window (27, Fig. 1) in front of the rotating mirror (22, Fig. 1), and the identical procedure was gone through again. It is clear that this is equivalent to conducting the test with the rotating mirror effectively locked. Any deflection of the thermo-relay galvanometer obtained in this way is ascribable to a deformation in some part of the apparatus outside the solenoid, and should be subtracted from the deflection observed in the magnetostriction test. Such effects were actually found. Their magnitude varied from zero to about 1 mm, i.e., they were equivalent to a magnetostriction of from zero to 2.5×10^{-8} . The probable cause of this stray effect will be discussed later.

A second correction which was required was for a shift of the zero-reading of the thermo-relay galvanometer. The zero-reading was shifted from 0.9 to 1.0 mm by the vibration under full load of the motor-generator set operating the solenoid. To measure the zero-shift the thermo-relay lamp was turned out, so that the thermo-relay became inoperative, and the current in the solenoid was built up in the usual manner. The zero-shift correction was not variable but, nevertheless, it was determined anew for each magnetostriction test.

The two corrections discussed above had opposite signs in most instances, so that they practically nullified each other. The thermo-relay galvanometer did not show any transient effect ascrib-

able to the stray field of the solenoid.

DISCUSSION OF CORRECTIONS AND ERRORS

(A) Imperfections in Crystals

There is little question as to the perfection of the crystals used in this investigation, so long as only crystals of pure bismuth are concerned. The only departure occurred in the case of the P-3 crystals, the principal axes of which should have been parallel to the axis of the rod, but were actually inclined at an angle of about 4 degrees. The work of Kapitza⁹⁾ shows that this introduced an error of about 0.3%, which is entirely negligible in the present instance.

In considering crystals which contain impurities purposely added to the bismuth, it must be pointed out that the amount of impurity as stated in the table of results, is merely the amount added to the melt from which the crystal was grown. It is known, however, from the work of Straumanis²⁴⁾, that there is little tendency for the separation of the impurity in the process of crystallization as long as the limits of solid solubility are not exceeded. The limit of solubility is higher in single crystals than in polycrystals. Its exact value is not known, but no difficulty was experienced in growing the crystals for this investigation, so that there is reason to believe that the limit of solid solubility was not transgressed.

As far as the distribution of the impurity along the axis of the rod is concerned, it is known that the impurity does not

travel along the axis of the rod in the process of crystallization, provided the solidification is fast enough, or the amount of impurity does not exceed certain limits. Dr. A. Goetz made a study of this subject on bismuth crystals by means of a microscopic examination of cleavage planes under polarised light. This work is not published yet. Straumanis²⁵⁾ studied the question in zinc crystals. Numerical data can be obtained from the work of Focke¹⁰⁾ on the susceptibility of bismuth crystals. Focke found that in a crystal of bismuth containing 2% (atomic) of lead, grown at the rate of 6 mm per minute, the magnetic anisotropy of both ends was practically the same, indicating that the same amount of impurity was contained in both ends. If the crystal, however, was grown at the rate of only 1 mm per minute, the end which crystallized first showed a magnetic anisotropy corresponding to only 1% of lead, while the end which crystallized last showed an anisotropy corresponding to 3% of lead.

Now, all the P-1 crystals used in this investigation were grown at speeds of about 6 mm per minute, so that there is no reason to question the uniformity of distribution of the impurity. The P-3 crystals, however, were grown at a speed of only 1 mm per minute. While it is not safe to extend to the P-3 crystals the results obtained by Focke on P-1 crystals, there is considerable reason to suspect that in these crystals the impurities are not distributed uniformly along the rod.

There is a mitigating factor, for the crystals used in this work were grown somewhat longer than necessary, and only the central portion was used, where the amount of impurity is more nearly correct. Of this central 11 cm actually used in the test, the central half contributes 60% to the magnetostriction, because of inhomogeneity of the magnetic field.

The net result of the above is, that, in the case of magnetostriction parallel to the principal axis (P-3 crystals), the curves showing the effect of impurities are drawn from points which represent the average magnetostriction for a certain range of impurity, rather than the magnetostriction for a specific amount of impurity. If the exact distribution of impurity in the crystal were known these curves could be corrected by a step by step method.

(B) Errors in calibration

(1) Sensitivity. The sensitivity calibration depends on a knowledge of the coefficients of thermal expansion of the crystals, which were measured by T. L. Ho to about 1%. Hence an uncertainty of about 1% in all the measurements results from this source.

The calibration can also be in error if the platinum resistance thermometer does not take a representative average of the air-temperature within the apparatus. This is not likely since the thermometer wire surrounds the crystal, and extends over its entire length. A more serious error may be introduced

by the fact that, because of greater heat capacity, the copper cups in which the crystal is soldered may be at an appreciably different temperature from the major portion of the crystal. This might introduce a heat-sink at the ends of the crystal, so that at the times when the thermal gradient of the crystal changes sign (Fig. 4), the average temperature of the crystal may be different from the average air temperature. It is difficult to make any estimate as to the magnitude of such an effect. It may be pointed out, however, that this would be a systematic error, which would not affect the curves showing the effect of impurities on magnetostriction, since magnetostriction in that case is expressed as a percentage of the magnetostriction in pure bismuth.

(2) Magnetic field. During the latter part of the investigation the solenoid became gradually short-circuited, so that the field intensity for a given current decreased in each succeeding test. Between calibrations of the solenoid the field intensity was calculated by interpolation in accordance with the voltage across the solenoid required to pass a given current. This leads to an uncertainty as to the magnetic intensity of the order of 2%. Since magnetostriction depends on the square of the field, the resulting error may be of the order of 4%.

(C) Errors in magnetostriction measurement

(1) Stray Effects. As already mentioned, when a mirror was attached firmly to the glass window (27, Fig. 1) in front of

the rotating mirror (22, Fig. 1), the application of the magnetic field produced a variable effect, equivalent to a magnetostriction of as much as 2.5×10^{-8} . It seems likely that the cause of this was a deflection of the filament in the thermo-relay lamp. This lamp was supplied with direct current and, hence, the filament might be deflected by the stray field of the solenoid. It is true that, in order to prevent this very effect, the lamp filament was focussed on a slit smaller than the image of the filament, rather than directly on the thermo-relay. Nevertheless, because of asymmetrical distribution of intensity in the image of the filament a shift of the filament would result in a shift of the intensity distribution of the slit, and would be equivalent to a motion of the slit. It was actually observed that this effect could be decreased by a careful adjustment of the filament image on the slit.

A stray effect which was more serious than the above, because it could not be corrected for, was an aperiodic motion of the thermo-relay galvanometer, reaching an amplitude as large as 1 mm, which existed independently of whether the beam of light was thrown on the thermo-relay by reflection from the rotating mirror, or from a fixed mirror. It is this background of motion which set the actual limit to the magnification used in this experiment. The motion can be seen on the records shown in Figs. 9, 10 and 11. The disturbance was at least three times as large before it was discovered that it could be reduced

by having a fan blow a stream of air across the path of the beam of light. The effectiveness of the fan is attributed to the breaking up of slowly varying temperature gradients in the air, which cause irregular diffraction of the light in air.

The effect described above results in a definite uncertainty in the measurement of magnetostriction records. Its effect is estimated at about 0.5 mm, equivalent to an uncertainty of about 1.3×10^{-8} in the magnetostriction. In the case of pure bismuth crystals tested in a field of 26,000 gauss, this introduces an error of about 5%. The percentage error is, of course, increased, if measurements are made in a field of lower intensity, or if the impurity decreases the magnetostriction.

(2) Magnetostriction of the frame. It is clear that the apparatus used in this investigation does not measure the absolute magnetostriction, but rather the difference between the magnetostriction of bismuth, and that of the quartz frame in which the crystal is mounted. Now, the magnetic susceptibility of quartz is so small that an appreciable magnetostriction is not to be expected. To check this, however, a magnetostriction test was made on a polycrystalline rod of copper. No measurable effect was obtained, showing that either the magnetostriction in quartz and copper is the same, which is not likely, or that neither of the two materials shows a magnetostriction measurable with the apparatus used.

(3) Mechanical stress in the crystal. In describing the

apparatus it was pointed out that the central quartz tube (14, Fig. 1), which forms an extension of the crystal, is held in place by four bronze wires attached to it radially. This method of mounting produces a stress in the crystal whenever the latter changes its length. It is the purpose of this section to determine whether this stress can produce a serious deformation of the crystal.

The force required to move the central quartz tube against the resistance of the four bronze wires was found to be 1 gr for a deflection of 2×10^{-5} cm, and was proportional to the deflection for a range at least eighty times as great. Since, in the magnetostriction test, the length of the crystal changes by about 3×10^{-6} cm, the force on the crystal is about 0.15 gr. Such a force, applied to a crystal with a section area of 4 sq.mm. would produce a strain of 0.5×10^{-8} , which is within the limits of sensitivity, though not within the limits of accuracy of the apparatus. No correction is needed under any circumstances, since an identical strain is applied in calibrating the apparatus by a temperature variation. The above effect is corrected automatically in the calibration.

(4) Effect of inhomogeneity of the field. In this investigation magnetostriction was measured in a magnetic field far from homogeneous (Fig. 5), while the usual meaning of the term magnetostriction means magnetostriction in a homogeneous field. Now, Kapitza⁹⁾ has shown that within the range of magnetic intensity

used in this experiment the magnetostriction is proportional to the square of the field. Hence, if we specify the field by its root-mean-square value taken along the crystal the magnetostriction has its usual significance.

A correction overlooked in the above is caused by the fact that a diamagnetic substance exposed to a non-homogeneous field is acted on by a force which tends to move it out of the field. In the case of a crystal mounted symmetrically in the field, as in this experiment, there is no resultant force, but the crystal experiences a tension, and a corresponding elongation. We proceed to calculate this strain:

The general expression for the force per unit volume on a substance which has no permanent magnetisation is

$$F = -\frac{H^2}{8\pi} \frac{\partial \mu}{\partial y} + \frac{\partial}{\partial y} \left(\frac{H^2}{8\pi} \tau \frac{\partial \mu}{\partial \tau} \right)$$

where F = force per unit volume in the y -direction

H = magnetic field intensity

μ = permeability

τ = density

Since $\frac{\partial \mu}{\partial y} = 0$, and $\frac{\partial \mu}{\partial \tau} = 4\pi x$, where x is the atomic susceptibility,

$$F = \frac{x\tau}{2} \frac{\partial}{\partial y} (H^2)$$

We put the origin at the center of the crystal, and measure y along the crystal. Also let L be the half-length of the crystal, and Y the modulus of elasticity. Then the strain at any point y is

$$\frac{dL}{dy} = -\frac{1}{Y} \int_L^y F dy = -\frac{x\tau}{2Y} (H^2 - H_L^2)$$

where H is a function of y , and H_L is the intensity at the end of the crystal. The average strain is obtained by integrating over the crystal, viz.:

$$\frac{\Delta L}{L} = \frac{1}{L} \int_0^L \frac{dL}{dy} dy = -\frac{x\tau}{2YL} \int_0^L (H^2 - H_L^2) dy = -\frac{x\tau}{2Y} (\bar{H}^2 - H_L^2)$$

where \bar{H} is the r.m.s. field intensity.

The effect is a maximum when the principal axis of the crystal coincides with the axis of the rod. Then

$$x = -1.04 \times 10^{-6} \quad 10)$$

$$1/Y = 1.62 \times 10^{-12} \quad 11)$$

The other constants are: $\bar{H} = 26,000$ gauss, $H_L = 17,000$ gauss,

$\tau = 9.8$. Hence

$$\Delta L/L = 3 \times 10^{-10}$$

This effect is of the order of 0.15% of the magnetostriction, and is totally negligible.

(5) Thermal Effects. Despite the water-jacket surrounding the apparatus it was found impossible to maintain the crystal at a uniform temperature during a magnetostriction test. This is not surprising, since the outside temperature of the solenoid increased during the test from 25 deg.C to about 50 deg.C. So long

however, as the temperature drift of the crystal remained uniform, no error was introduced into the measurement, since the temperature drift resulted only in an inclination of the base-line from which magnetostriction was measured. This can be seen on the records in Figs. 9, 10 and 11.

If, while the field is on, a change takes place in the rate of change of temperature, this can be recognized on the record by the fact that the inclination of the base-line is different before and after the field is established. A correction, however, cannot be made in any formal manner, but rather by a judicious interpretation of the record. Since at least four tests are made on each crystal, no serious error can arise from this source.

The temperature of the crystal is increased also when the magnetic field is established or destroyed, because of induction currents in the crystal. The energy developed per unit volume of a cylindrical conductor, in which a field H is established parallel to the axis of the cylinder is

$$E = \frac{r^2}{8\rho} \int \frac{\partial H}{\partial t} dH$$

where r is the radius of the cylinder, and ρ is the resistivity.

If we assume that the field intensity increases uniformly with time, the energy per unit volume is then

$$E = (r H)^2 / 8\rho t_0 ,$$

where t_0 is the time required to establish the field H .

In this experiment t_0 is about 10 seconds, but the field

does not increase linearly with time. We shall certainly over-estimate the correction if we put $t_0 = 1$ in the formula above. In this case the energy developed in a bismuth crystal, 3 mm in diameter, when a field of 26,000 gauss is established, is only 16 ergs per cc. The resultant rise in temperature is 10^{-6} deg.C, and the corresponding elongation per unit length is 2×10^{-11} , which is entirely negligible.

A more important thermal effect, first pointed out by Langevin¹⁴), is the change in the temperature of a substance on magnetisation, on the assumption of an adiabatic process. We shall calculate this effect in the manner outlined by Houston¹⁵).

We regard the state of the crystal as a function of its temperature, T , and magnetic field H . If T and H are changed by infinitesimal amounts, the heat, q , of the body changes by

$$dq = C dT + a dH.$$

Hence
$$dS = (C/T)dT + (a/T)dH,$$

where S is the entropy. If B is the magnetic induction, the work done on the crystal per unit volume is

$$dw = H dB/4\pi$$

Hence, if U be the internal energy,

$$dU = dq + H dB/4\pi$$

Expressing dq and dB in terms of dT and dH ,

$$dU = \left(C + \frac{H}{4\pi} \frac{\partial B}{\partial T} \right) dT + \left(a + \frac{H}{4\pi} \frac{\partial B}{\partial H} \right) dH$$

Since dS and dU are complete differentials, we obtain by means of the reciprocity relations the two equations

$$\frac{\partial \epsilon}{\partial H} + \frac{1}{4\pi} \frac{\partial B}{\partial T} = \frac{\partial a}{\partial T}$$

and

$$\frac{1}{T} \frac{\partial \epsilon}{\partial H} = \frac{1}{T} \frac{\partial a}{\partial T} - \frac{a}{T^2}$$

Combining the two above equations,

$$\frac{a}{T} = \frac{1}{4\pi} \frac{\partial B}{\partial T} = H \frac{\partial x}{\partial T}$$

where x is the susceptibility. We substitute the value of a from the above equation in the original expression for dq :

$$dq = C dT + H T \frac{\partial x}{\partial T} dH$$

If the process is adiabatic dq is zero. Hence

$$\frac{dT}{dH} = - T \frac{H}{\epsilon} \frac{\partial x}{\partial T}$$

From this equation one can calculate the change in temperature on adiabatic magnetisation, provided the law of the variation of x with T is known. Now, Kapitza¹⁷⁾ has found that in the case of bismuth crystals the variation of x with T obeys the law

$$x = x_0(1 - \alpha T),$$

where x_0 and α are independent of the temperature.

Therefore $dT/dH = T H x_0 \alpha / C$

and $\Delta T = T H^2 x_0 \alpha / 2C$

It can be seen from the original equation for dq that C is approximately the specific heat. If C is expressed in ergs per gram per deg.C, the other quantities in the equation can be expressed in absolute units.

If we use Kapitza's values of x_0 and α , and assume a magnetic field of 26,000 gauss, the change in length of a bismuth crystal, resulting from the above change in temperature, is as given below:

Parallel to trigonal axis (P-3 crystals): $-\Delta L/L = -1.2 \times 10^{-9}$

Perpend. " " " (P-1 " "): $-\Delta L/L = -2.4 \times 10^{-9}$

These figures pertain to an adiabatic process, so they represent the upper limit of the thermal elongation. In any case, even the greater of the two values is barely on the border of sensitivity of the apparatus used, since it is equivalent to a galvanometer deflection of 0.1 mm. The correction is therefore neglected.

(D) Summary

Reviewing the sources of error, we find that in the case of a crystal of pure bismuth, tested in a field of 26,000 gauss, the probable error arising from the uncertainty in the thermal coefficient of expansion is 1%, the uncertainty caused by the calibration of the field is about 4%, the error of reading the

records is about 5%. The final result is in doubt by perhaps 10%, which is amply accurate enough for an experiment of this kind.

In the case of crystals tested in weaker fields, or in cases where the magnetostriction is reduced by the addition of impurities to the bismuth, the percentage error is, of course, greater. The first two sources of error still result in an uncertainty of about 5%, but the error of reading the galvanometer records is fixed in magnitude, and, hence, expressed in per cent, it is inversely proportional to the magnetostriction.

MAGNETOSTRICTION IN SINGLE CRYSTALS OF PURE BISMUTH

In the case of pure bismuth magnetostriction tests were made on five crystals. The results are given in Table I, which is self-explanatory. The most striking fact about the results is that magnetostriction is positive (increase in length) parallel to the trigonal axis (P-3 crystals), and negative at right angles to the trigonal axis (P-1 crystals).

Since it was not possible to check all crystals with exactly the same field intensities, the best comparison between the crystals is obtained from the moduli of magnetostriction, m . The agreement between each pair of crystals of like orientation is extremely close. The difference between the moduli of the two P-3 crystals is only 1%; the difference between the two P-1, 0° , crystals is 7%.

TABLE I

LONGITUDINAL MAGNETOSTRICTION IN BISMUTH SINGLE CRYSTALS

PURE BISMUTH

All measurements at 25°C.

DATE	CRYSTAL ORIENT*	DESIGN. OF BISMUTH	TEMP. COEFF. OF EXP.	SENSIT. FACTOR	MAGN. FIELD	LONGIT. MAGNETO-STRICTION	MODULUS OF MAGNETO-STRICT*
			$\times 10^6$	$F \times 10^8$	Gauss	$\Delta L/L \times 10^8$	$m \times 10^{16}$
1932							
6-10	P-1,30°	H	11.6	9.7	13,700 19,300 25,900	- 5. -10. -22.5	-6.65
6-13	P-1,0°	H	11.6	9.8	14,200 20,100 26,000	- 6. -15.5 -24.5	-7.3
6-15	P-3	H	15.9	9.5	13,600 20,500 26,000	+ 6.5 +13. +19.5	+5.7
6-30	P-1,0°	J	11.6	9.9	25,750	-22.5	-6.8
7-31	P-3	J	15.9	9.6	12,350 18,700 24,000	+ 6.5 +11. +16.	+5.65

* See List of Principal Symbols.

The modulus of the P-1, 30° , crystal is within the limits of experimental error of the moduli of the P-1, 0° , crystals. The accuracy of the present investigation is not sufficient to distinguish between the two subsidiary orientations. Hence no further tests were made on crystals of the P-1 30° , orientation.

Fig. 12 shows the magnetostriction values from Table I, plotted against the magnetic field, and compared with the recent results of Kapitza⁹⁾, although the latter's work is not accurate in the range of magnetic fields here represented. It is seen that there is good agreement. A comparison of the two investigations can also be made on the basis of the moduli of magnetostriction, as shown by the table below:

MODULI OF MAGNETOSTRICTION IN PURE BISMUTH

25 deg.C., 25,000 gauss

Crystal orientation	P-1, 0°	P-3
Modulus "m" - this exp.	-7.05×10^{-16}	5.7×10^{-16}
" " - Kapitza	-7.3	6.5
Difference	3.5%	11.5%

The agreement is seen to be quite good when one considers that the present work does not claim an accuracy of over 10%, and Kapitza considers his limiting error as about 8% in his strong fields, and probably less in the range which is here represented.

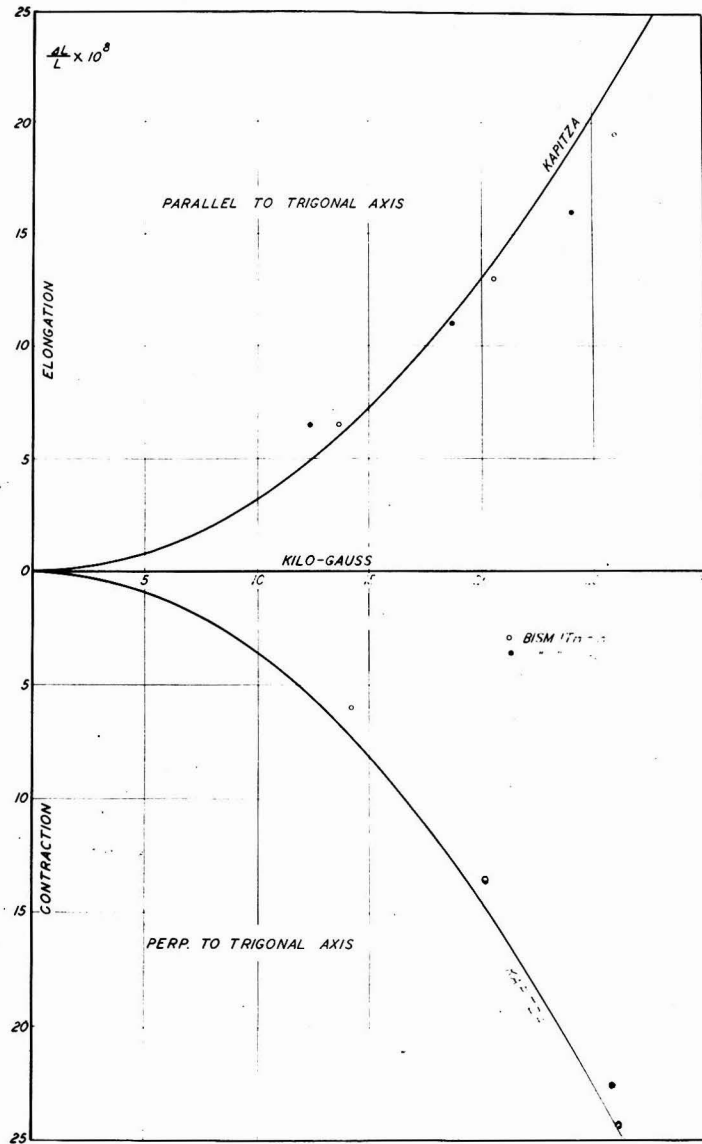


Fig. 12.

Magnetostriction in single crystals of pure bismuth,
25 deg. C.

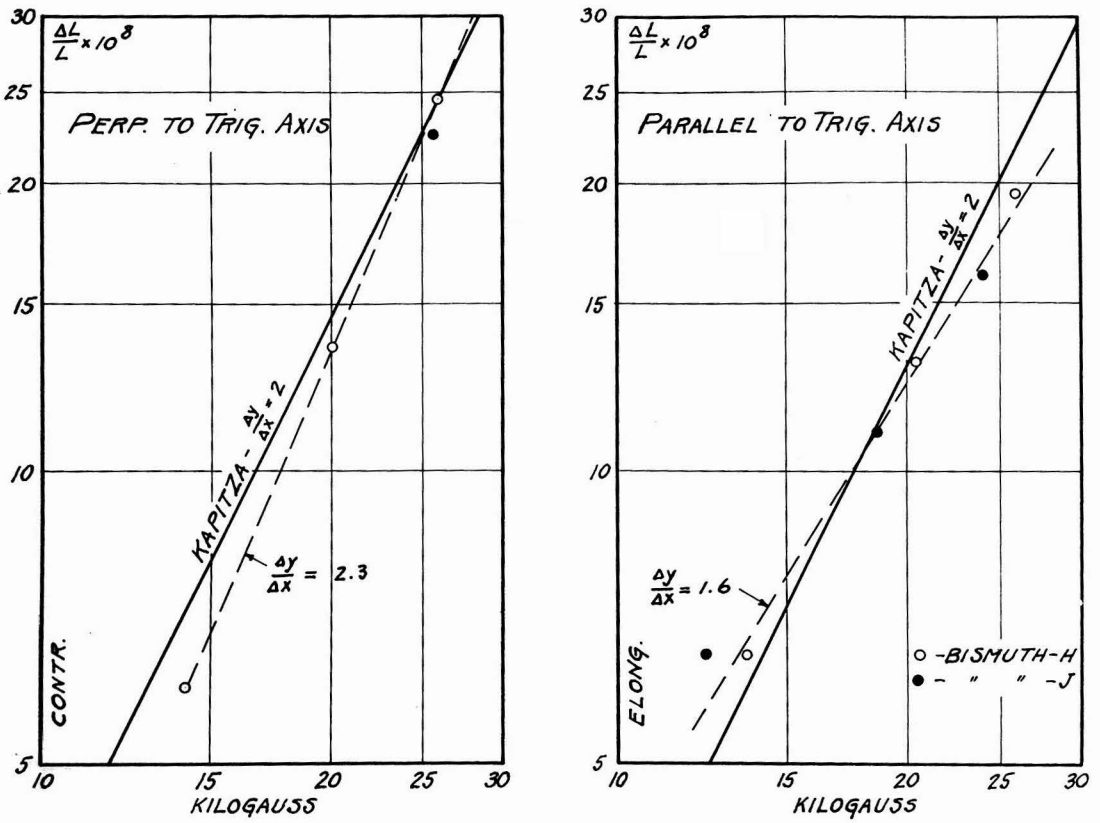


Fig. 13.

Magnetostriction in single crystals of pure bismuth; 25 deg. C.

In order to check the theoretical expression for magnetostriction as a function of the magnetic field, the data of Table I were plotted on a logarithmic scale in Fig. 13. It is seen that the points lie practically on straight lines. From the inclination of the lines one obtains the equation

$$\Delta L/L = k H^n$$

where $n = 2.3$ for P-1 crystals (perp. to trig. axis)

$n = 1.6$ " P-3 " (parallel to trig. axis)

$k = \text{constant}$, dependent on crystal orientation

This appears to be valid between 15 and 25 Kilogauss.

Kapitza⁹⁾ obtained $n = 2$, valid at least up to 100 Kilogauss. The present work, however, does not actually contradict Kapitza's, since the accuracy of both investigations drops so rapidly with decreasing magnetic intensity, that a definite determination of the exponent of H is not possible in weak fields.

THE EFFECT OF IMPURITIES ON MAGNETOSTRICTION IN BISMUTH

In order to determine the effect of foreign atoms on the magnetostriction of a bismuth crystal, tests were made on 22 crystals of bismuth containing various amounts of tin, lead or tellurium. These particular elements were selected, since they go into solid solution in bismuth, and their atoms differ from bismuth only by one valency electron (Pb), or by both a complete electron shell and a valency electron. The effect of these ele-

TABLE II
 LONGIT. MAGNETOSTRICTION IN BISMUTH SINGLE CRYSTALS

THE EFFECT OF IMPURITIES

All measurements at 25°C

DATE	CRYSTAL ORIENT*	DESIGN. OF BISMUTH	TYPE OF IMPURITY	AMOUNT OF IMP.***	TEMP. CORR. OF EXPANSION	SENS. FACTOR $\times 10^8$	MAGN. FIELD Gauss	$\frac{\Delta L}{L} \times 10^8$	MODULUS OF MAGNETOSTR.*	PER CENT MAGNETOSTR.***
1952										
6-13	P-1, 0°	H	-	-	11.6	9.8	26,000	-24.5	-7.3	100
15	P-3	"	-	-	15.9	9.5	26,000	+19.5	+5.7	100
18	P-1, 0°	"	Te	0.3	11.6	8.7	25,750	-6.5	-1.9	26
22	"	"	Te	0.2	11.6	8.6	25,750	-7	-2.2	30
24	"	"	Te	0.1	11.6	8.85	25,750	-9.5	-2.9	40
30	"	J	-	-	11.6	9.9	25,750	-22.5	-6.8	100
7-3	"	"	Te	0.05	11.6	9.1	25,750	-11.	-3.3	48
5	"	"	Sn	0.1	11.6	8.6	25,750	-17.	-5.0	74
12	"	"	Te	0.01	11.6	8.75	25,750	-19.	-5.7	83
13	"	"	Sn	2.5	12.5	10.7	25,750	+34	+10.3	-151
14	"	"	Sn	1.0	12.0	8.5	25,750	+19	+5.8	-86
17	"	"	Sn	5.0	12.9	9.5	25,750	+33.5	+10.1	-149
18	"	"	Sn	0.5	11.6	11.1	25,750	+12	+3.7	-54
21	P#3	"	Sn	0.9	15.0	10.2	25,750	+12	+3.6	64
22	"	"	Sn	4.4	14.7	9.8	25,750	+22	+6.8	120
24	"	"	Te	0.09	15.9	12.8	25,750	+15	+4.5	80
27	"	"	Te	0.24	15.9	9.6	25,750	+5	+1.6	29

(continued on next page)

DATE	CRYSTAL ORIENT.	DESIGN. OF BISMUTH TYPE OF IMPURITY	AMOUNT OF IMP. %	TEMP. CONTR. OF EXPANSION $\times 10^6$	SEMS. FACTOR $\times 10^3$	MAGN. FIELD Gauss	LONGIT. MAGNETOSTR. $\frac{\Delta L}{L} \times 10^8$	MODULUS OF MAGNETOSTR. $\times 10^6$	PER CENT MAGNETO-STRIC. %
7-29	P-3	J Pb	1.0	16.4	9.7	24,000	+14.5	+ 5.1	90
31	"	" -	-	15.9	9.6	24,000	+16	+ 5.65	100
8-4	"	" Te	0.09	15.9	9.45	23,450	+10.5	+ 3.8	67
14	"	" Sn	0.44	15.9	9.6	22,650	+12.5	+ 4.8	86
15	"	" Sn	2.4	15.2	10.7	21,850	+13.5	+ 5.7	102
28	"	" Pb	2.56	16.5	10.2	21,750	+14	+ 5.9	104
30	P-1,00	" Pb	1.0	12.2	9.3	21,000	- 6	- 2.8	42
31	"	" Pb	2.56	12.8	9.9	20,800	+ 5.5	+ 2.5	- 36
9-3	"	" Pb	4.9	13.1	10.2	20,400	+15	+ 7.2	-105
6	P-3	" Pb	4.9	16.7	10.7	20,400	+ 9	+ 4.4	78
10	"	" Pb	2.56	16.5	16.3	20,400	+11.5	+ 5.6	99

* See List of Principal Symbols

** Expressed in atomic per cent, i.e., number of foreign atoms per 100 atoms of bismuth

*** Modulus of magnetostr. expressed in per cent of modulus for crystal of same orientation, but without the impurity

ments on the susceptibility of bismuth is known from the work of Focke¹⁰⁾. The results of the magnetostriction tests are given in detail in Table II.

The crystals were tested only in the maximum available magnetic field. Since this was not always the same, the effect of the impurities can be obtained only from a comparison of the moduli of magnetostriction, which are listed in the second column from the end in Table II. The last column of the table gives the "per cent magnetostriction", which is obtained by dividing the actual modulus of a crystal by the modulus of the crystal of the same orientation, but containing no impurity. The "per cent magnetostriction" is plotted against the impurity in Fig. 14. The amount of the impurity is expressed in atomic percentage, i.e., as the number of foreign atoms per hundred atoms of bismuth.

An examination of Fig. 14 will show that lead and tin exercise a particularly striking influence on magnetostriction perpendicular to the trigonal axis (P-1 crystals). About 0.4% of tin, or about 2% of lead reduce the magnetostriction to zero, and greater amounts of these elements actually reverse the sign of the effect. It should also be pointed out that the curves for lead and tin are identical except for the horizontal scale. It requires almost exactly five times as much lead as tin to change the magnetostriction perpendicular to the trigonal axis by a given amount. The same relation between lead and tin was found by Focke¹⁰⁾ in his measurements of susceptibility.

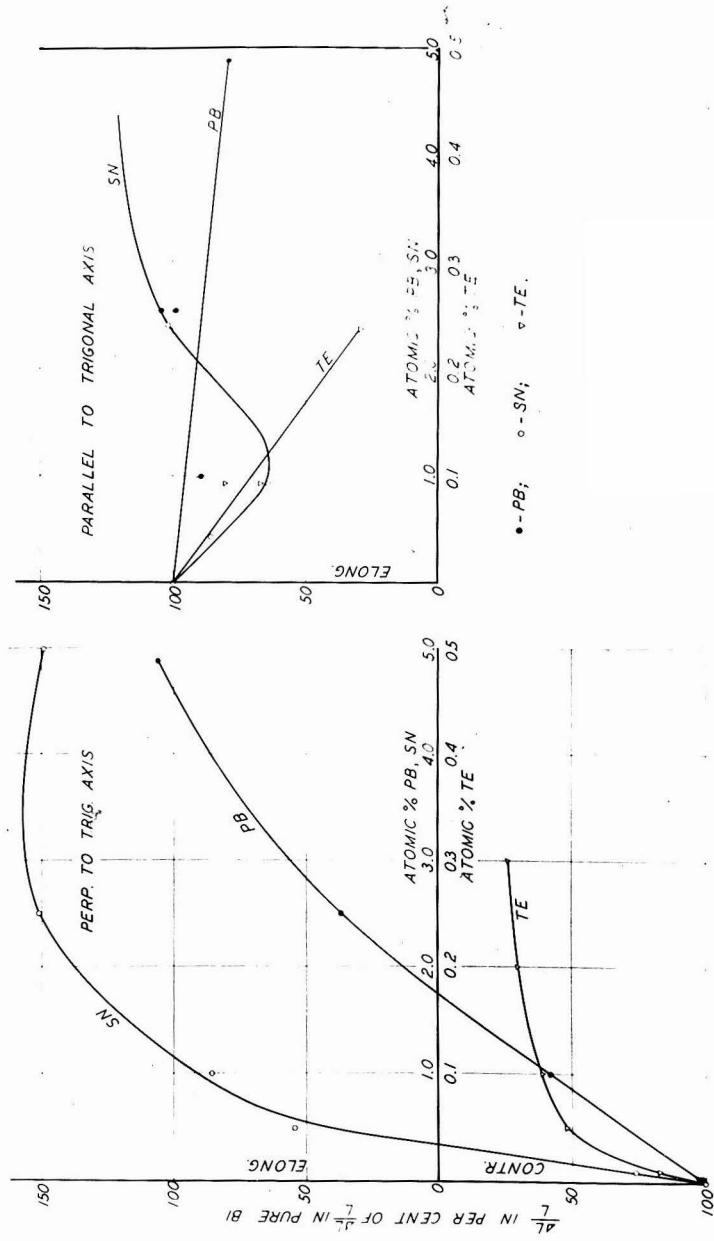


Fig. 14. - The effect of impurities on magnetostriction in bismuth; 25 deg. C.

The effect of lead and tin on magnetostriction parallel to the trigonal axis (P-3 crystals) is much smaller than in the preceding direction, and more complicated in character. The influence of lead is still much smaller than that of tin, but the effect here is so small that a definite conclusion cannot be reached as to the ratio of the effects of the two elements.

The influence of the electro-negative element tellurium is different in character from that of lead and tin, since no reversal takes place in the sign of magnetostriction perpendicular to the trigonal axis, and the effect is quite large parallel to the trigonal axis.

THE MODULUS OF MAGNETOSTRICTION IN THE LIGHT OF THE THERMODYNAMIC THEORY.

As shown in the section on the thermodynamic theory of magnetostriction, the modulus of magnetostriction in bismuth is practically equal to the rate of change of susceptibility with stress, i.e.,

$$m = \partial x / \partial p,$$

where the susceptibility must be measured in the same direction as the stress. If the crystal is subjected to a stress p , the corresponding change in susceptibility is

$$\Delta x = \int \frac{\partial x}{\partial p} dp = \int m dp.$$

Kapitza⁹⁾ has shown that in bismuth m is practically independent

of p . Hence

$$\Delta x = m p$$

and the percentage change in x is $100 mp/x$.

The elastic limit of a bismuth crystal is greatest along the trigonal axis, where its value is about 3.5×10^7 dynes per sq.cm. The maximum of the ratio m/x obtains also in the direction parallel to the principal axis, where $x = -1.05 \times 10^{-6} \times 9.8$, and $m = 5.7 \times 10^{-16}$. The percentage change in susceptibility is then about 0.2%. Experiments in that direction would be of interest, if only to check the theory of magnetostriction. It is seen, however, that to measure accurately a 0.2% change in susceptibility under a heavy loading would be extremely difficult, so that the measurement of magnetostriction still presents the best method of studying the effect of stress on susceptibility.

CONCLUSION

The experiments described in this paper furnish a close check on some of the work of Kapitza on magnetostriction in bismuth. This is of some importance, since the validity of Kapitza's results might be questioned, principally on the ground that they were obtained in rapidly varying fields.

The influence of impurities on magnetostriction in bismuth is studied in some detail. It is shown that small amounts of certain impurities produce a very large effect, since, at right

angles to the trigonal axis, one atom of tellurium per two-thousand of bismuth reduces the magnetostriction to one-half, and one atom of tin per hundred of bismuth completely reverses the magnetostriction.

Apart from its intrinsic interest, the work on magnetostriction may be of fundamental value, since the moduli of magnetostriction represent the variation of susceptibility with stress, or with its equivalent distortion of the crystal lattice. A study of the variation of magnetostriction with impurities is equivalent to the study of the influence of impurities on the manner in which a distortion of the crystal lattice affects its magnetisation. Since an adequate theory of crystal diamagnetism must proceed from the properties of the crystal lattice, it is evident that a knowledge of the effect of a distortion on the magnetic properties of the lattice is apt to be of use in the formulation of a theory.

In conclusion I wish to express my thanks to Professor A. Goetz for suggesting this investigation and for his advice during the progress of the work, to Dr. A. S. King for the permission to use the solenoid at the Mt. Wilson Laboratory, and to Dr. Focke and Mr. Darlington for the preparation of a great part of the crystals used in this work.

SUMMARY

The paper describes the measurements of longitudinal magnetostriction in single crystals of pure bismuth, and bismuth

containing known amounts of impurities. The measurements were made in a field of about 25,000 gauss. If a modulus of magnetostriction "m" is defined by the equation $\Delta L/L = \frac{1}{2} mH^2$, the values of "m" for pure bismuth are found to be $+5.7 \times 10^{-16}$ parallel to the trigonal axis, and -7.0×10^{-16} perpendicular to the trigonal axis. These figures are in good agreement with results of Kapitza.

The influence of the addition of lead, tin and tellurium to the bismuth crystals is studied in detail. The addition of tin or lead is found to produce the greatest effect at right angles to the trigonal axis, where 0.4% of tin, or 2% of lead reduce the magnetostriction to zero, and greater amounts actually reverse the sign of the magnetostriction. Tin and lead have a much smaller effect on the magnetostriction parallel to the trigonal axis. In general, one atom of tin produces the same effect as five atoms of lead.

The influence of tellurium is different in character from that of lead and tin, and much smaller amounts of the impurity produce large changes in magnetostriction. No reversal of the sign of magnetostriction is found. The order of magnitude of the effect of tellurium on magnetostriction is the same in the two principal crystal orientations.

REFERENCES

- 1) Joule, Sturgeons Ann. of El., 8, 219
- 2) Aubel, Phys. Rev., 16, 60, 1903
- 3) Bidwell, Phil. Trans., 179, 205, 1888
Nature, July 6, 1899, p. 222
- 4) Wills, Phys. Rev., 15, 1, 1902.
- 5) Hobbie, Phys. Rev., (2), 19, 456, 1922
- 6) Schulze, Zeits. f. Phys., 50, 448, 1928
- 7) Kapitza, Nature, 124, 53, 1929
- 8) Bryan and Heaps, Phys. Rev., 37, 466, 1931
- 9) Kapitza, Proc. Roy. Soc., A 135, 537, 1932
- 10) Focke, Calif. Inst. Techn., Thesis 1932
- 11) Bridgman, Proc. Amer. Ac. Arts & Sc., 60, 305, 1925, also
Int. Crit. Tables, III, 49
- 12) McKeehan and Cioffi, Phys. Rev., 28, 146, 1926
- 13) Goetz, Phys. Rev., 35, 193, 1930
- 14) Langevin, Ann. Chim. et Phys., 5, 123, 1905
- 15) Houstoun, Phil. Mag., 21, 78, 1911
- 16) Leduc, Comp. Ren., 152, 853, 1911
- 17) Kapitza, Proc. Roy. Soc., 131, 270, 1931
- 18) Grimaldi, Journ. de Phys., VIII, 552, 1889
- 19) Aubel, Journ. de Phys., I, 424, 1892
- 20) Knott, Nature, June 22, 1899, p. 191
- 21) Hergenrother, Physics, 2, 63, 1932
- 22) Goetz and Focke, Phys. Rev., 37, 1044, 1931

- 23) Goetz and Hasler, Phys. Rev., 36, 1752, 1930
- 24) Straumanis, Z. physikal Chem., A 148, 112, 1930
- 25) Straumanis, Z. anorg. u. allgem. Chem., 180, 1, 1929