the Bi-Pb crystals[9] in the region of the eutectic melting point since the corresponding point for the Bi-Ag system lies at 260°C. Since changes of this type apparently do not affect the regions of the lattice capable of diffraction, they should not be reflected in x-ray measurements.

Our observations establish thus a support for the hypothesis of "decrystallization" by Goetz and Hergenrother[2] which attributes any deviation of the macroscopic qualities from the crystal lattice as seen by x-rays to disturbances caused by foreign atoms even if they are soluble. The mentioned hypothesis suggests, however, a divergence of the two expansions (i.e., a decline of the macroscopic dilatation) even for ideally pure material. The present results do not disprove this possibility since the region of such a decline may be restricted to the very close neighborhood of the melting point which is inaccessible due to plastic deformation of the specimen in the gravitational field.

The authors are indebted to Dr. M. F. Hasler for the spectroscopic and polarographic analyses and to him and Mr. R. C. Kendall for aid in growing the crystals and valuable discussions during the course of the work.

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[9] A. Goetz, J. W. Buchta and T. L. Ho, Phys. Rev. **46**, 538 (1934).

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The Magnetostriction of Pure and Alloyed Bi Single Crystals*

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The existence of a magnetostrictive effect (Joule effect) in nonferromagnetic substances, first demonstrated by Kapitza for large transient fields, is here shown for steady fields of moderate (20 to 25 kg) values. Pure (99.97 percent) Bi single crystals and crystals with dissolved foreign atoms are used. A recording dilatometer permitted measurements of a change in length of 2.5×10^{-7} cm. The sum of errors amounted to approximately 10 percent. The modulus of magnetostriction (m) is defined by $\Delta l/l=\frac{1}{2}mH^2$. For pure Bi crystals $m=+5.7\times10^{-16}$ (elongation) parallel to trigonal axis and $m=-7.0\times10^{-16}$ (contraction) normal to trigonal axis. Bi crystals with Pb, Sn and Te in concentration within the solubility range were studied. Sn and Pb (electropositive) first cause the contraction normal to the trigonal axis to diminish and finally with increasing concentrations, cause an elongation, Sn being four times as effective as Pb. Parallel to the axis small concentrations of Sn decrease the elongation, larger concentrations increase the elongation. The effect of Pb in this direction is small. Te (electronegative) produced a much larger specific effect but no change in sign. The effect was of the same order of magnitude for the two principal crystal orientations. The data are discussed with special reference to the influence of foreign atoms on the magnetic susceptibility, studied previously by Goetz and Focke. It was found that the change of the stress coefficient of the susceptibility with the concentration of foreign atoms *normal* to the principal axis is inversely proportional to the concentration and furthermore: the variation of the stress coefficient with the concentration is nearly equal to the variation of the susceptibility at higher concentrations, in other words the stress coefficient of the susceptibility is proportional to the susceptibility itself. It is furthermore concluded that the results presented justify the previous assumption of the existence of two types of insertion of foreign atoms in the crystal lattice, i.e., selective adsorption for small concentrations and volume absorption for larger concentrations.

I. INTRODUCTION

THE search for magnetostrictive effects in non-ferromagnetic materials was begun soon after the discovery by Joule in 1847 of the effect in ferromagnetic materials. Aubel[1] in his review quotes a number of attempts[2–6] to detect the phenomenon. All gave negative results as did more recent work of Hobbie,[7] Schulze[8] and Bryan and Heaps.[9] Kapitza[10, 11] was the first

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[*] Partly contained in: A. Wolf, Thesis, Cal. Inst. of Tech. 1933; A. Wolf and A. Goetz, Phys. Rev. **43**, 213 (1933).

[1] Aubel, Phys. Rev. **16**, 60 (1903).

[2] S. Bidwell, Phil. Trans. **179**, 205 (1888).

[3] Grimaldi, J. de physique **8**, 552 (1889).

[4] Aubel, J. de physique **1**, 422 (1892).

[5] Knott, Nature **61** (1899).

[6] A. P. Wills, Phys. Rev. **15**, 1 (1902).

[7] J. R. Hobbie, Phys. Rev. **19**, 456 (1922).

[8] A. Schulze, Zeits. f. Physik **50**, 448 (1928).

[9] A. B. Bryan and C. W. Heaps, Phys. Rev. **37**, 466 (1931).

[10] P. Kapitza, Nature **124**, 53 (1929).

[11] P. Kapitza, Proc. Roy. Soc. **A135**, 537 (1932).

to observe a positive result for Bi crystals. He used extreme fields (250–300 kg) of brief duration (10^{-2} sec.), thus detecting the small effect which the previous workers had failed to find.

This investigation is closely related to the work on crystal-diamagnetism on Bi crystals by Goetz and Focke[12–15] where a quantitative study of the influence of foreign atoms inserted into a metallic crystal lattice was made. It is thus of interest to investigate in what manner the changes of susceptibility caused in a crystal by inserted admixtures are reflected in the magnetostrictive effect; as such this investigation follows the lines of the general research program in this laboratory.

An additional purpose was to supplement the results of Kapitza concerning Bi crystals in a stationary magnetic field of moderate intensity (about 25 kg) in contradistinction to Kapitza's transient field of high intensity.

II. THE APPARATUS

(a) Method of measurement

The magnetostrictive effects in Bi are very much more difficult to measure than those in ferromagnetic substances. With fields of about three thousand gauss, the effect ($\Delta l/l$) in Ni is of the order of 3×10^{-5}, in Bi it is of the order of 3×10^{-9}. With a powerful solenoid producing a magnetic field of 25 kg the effect is still 100 times smaller than the magnetostriction of a ferromagnetic material in a moderate field. The extraneous disturbances on the apparatus produced by increasing the magnetic field are augmented to a marked extent. These disturbances are, principally the heating, transient currents induced by the field, vibration of the necessary rotating machinery, etc.

The essentials of the method of measurement are shown in Fig. 1. The change in length of the crystal *Cr* relative to that of a neutral material *N* rotates the mirror *M*. A beam of light from a fixed slit is reflected by the mirror and then focussed on the Moll-thermorelay *Th*. This is a differential thermocouple, Constantan *C* between copper *Cu* ribbons of low heat capacity (1μ thick) mounted in an evacuated glass bulb. The bulb is mounted on a micrometer stage and may be adjusted so that the beam of light from the mirror *M* heats each junction *C–Cu* equally. A slight displacement of the beam from this position results in a current through the galvanometer *G*.

The sensitivity of the arrangement depends upon the intensity of the light and the sensitivity of the galvanometer. As used, a motion of about 0.0007 mm of the spot of light gave a galvanometer deflection of 1 mm. The magnification of the optical lever was about 300 times, giving a total magnification of 1 : 400,000. With crystals 10 cm long a strain of 2.5×10^{-8} corresponded to 1 mm on the galvanometer scale.*

In addition to high sensitivity, the method offers advantages over microscopic or telescopic methods in that the readings can be recorded photographically. Also there is no indeterminacy caused by diffraction. The thermorelay integrates over the total beam and is not handicapped by a limited "resolving power." The image on the ribbon was 2–3 mm wide. The lack of mechanical magnifying levers made the set-up insensitive to mechanical vibration and permitted a 500 kw motor generator set to be located in the same room.

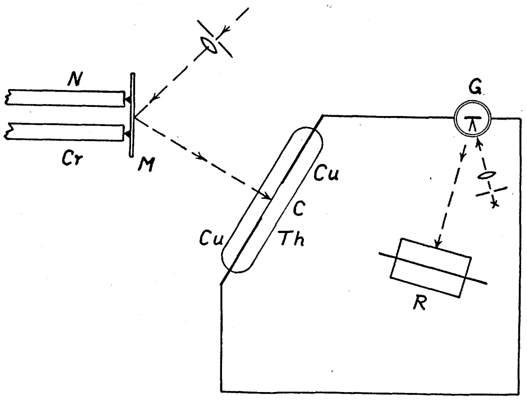

FIG. 1. Scheme of the magnetostriction—dilatometer. (*Cr*, crystal; *N*, neutral frame; *M*, mirror; *Th*, thermorelay; *G*, galvanometer; *R*, photographic recorder.) The full drawn line indicates the electric recording circuit, the dashed lines the optical paths.

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[12] A. B. Focke, Phys. Rev. **36**, 319 (1930).
[13] A. Goetz and A. B. Focke, Phys. Rev. **38**, 1569 (1931).
[14] A. Goetz and A. B. Focke, Science **74**, 603 (1931).
[15] A. Goetz and A. B. Focke, Phys. Rev. **45**, 170 (1934).

* It may be mentioned that an interferometer method could hardly be used for these experiments since the entire effect under investigation would have produced a shift of only one-tenth of a fringe in the visible region.

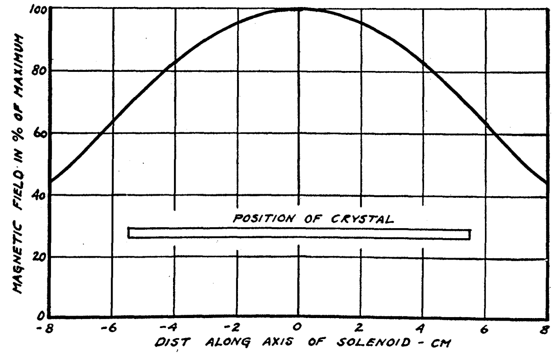

FIG. 2. Longitudinal field distribution along the axis of the solenoid.

(b) The magnet

The magnet used was a large 500 kw solenoid installed at the physical laboratory of the Mount Wilson Observatory constructed by Dr. J. A. Anderson. It consists of two coaxial coils of heavy copper tape which are connected parallel. The coils are enclosed in a brass shell leaving a central opening 2 inches in diameter. The cooling medium is transformer oil pumped at high speed through the interspace of the windings and through pipe slings immersed in a large water tank. The maximum current for which the solenoid is designed is 4000 amp. at 125 volts, which is supplied by a motor generator set mentioned above. The maximum field at the center of the coil is 28 kg, since however the coil is short the inhomogeneity of the field is large as shown in Fig. 2.

(c) Description of the dilatometer

The essential part of the apparatus is the framework in which the crystal is mounted, and the arrangement whereby the magnetostriction is transformed into the rotation of a mirror. This part of the apparatus, is shown in Fig. 3.

A brass block (1) is held rigidly in the wooden piece (2), which in turn is bolted to an outside wooden framework, not shown in Fig. 3. Two fused quartz tubes (3) are cemented in the brass block. Aluminum disks (4 to 10) are cemented to the quartz tubes, forming a rigid frame. The disk (9) holds a copper cup (11) in which one end of the crystal (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 disk (4). This feature of the apparatus is best seen in the section in the lower center of Fig. 3. 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 framework. 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 on the lower right of Fig. 3.

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. It can be readily seen that a change in the length of the crystal results in a horizontal 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 (see later) it was necessary to raise the temperature of the crystal by about 0.2°. This could be accomplished by means of a heating coil (23) extending over the full length of the crystal and being conducted through the holes in the aluminum disks. 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 disks (5, 6, 7, 8). A section showing the mica frames can be seen on the lower left of Fig. 3. 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

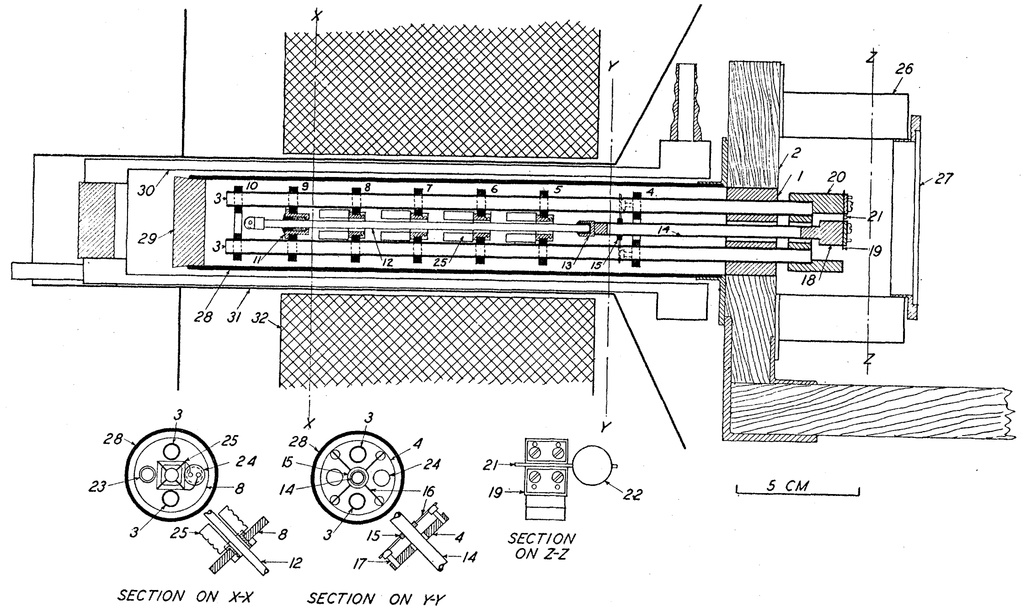

FIG. 3. Detail of the magnetostriction dilatometer.

thermometer also is needed for purposes of calibration.

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 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 on the figure. The optical system (Fig. 4) consists of a series street-lighting lamp A which is the source of energy for operating the thermorelay G. C is a horizontal slit, B, D are convex lenses. The cylindrical lens F is placed just in front of the thermorelay with its axis parallel to the ribbon in the thermorelay.

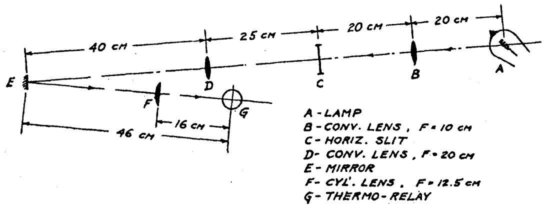

FIG. 4. Optical path between dilatometer and thermorelay.

The deflection of the galvanometer in the thermorelay circuit is recorded in a photographic recorder (Fig. 1) driven by a clockwork. A timing device makes a mark on the paper at intervals of 15 seconds.

III. THE CRYSTALS

The crystals used for this investigation had to be very uniform over a considerable length. They were grown after the method described by Goetz[16] and Goetz and Focke.[15] They were rods 2–3 mm in diameter and at least 120 mm long.

The metal was the brand of the Merck Chemical Co. Two separate lots designated as Bi H and Bi J were used. They are presumed to have not more than 0.03 percent impurities or found in lots E and F which were used in the magnetic measurements[15] since H and J had the same magnetic anisotropy. A spectroscopical analysis of E and F has been published.[15]

Two principal crystallographic orientations were studied. Following a designation given previously[17] P_1 crystals had the trigonal axis

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[16] A. Goetz, Phys. Rev. **35**, 193 (1930).

[17] A. Goetz and M. F. Hasler, Phys. Rev. **36**, 1752 (1930).

normal to the axis of the rod. For this case two variations of second order are possible: (a) One of the binary axis [111] in plane with the axis of the rod (P_1 0°); (b) one of the binary axis [111] normal to the axis of the rod (P_1 30°).

The other orientation (P_3) had the trigonal axis parallel to the axis of the rod, no secondary variations are possible in this case in a field symmetrical to the axis of the rod.

IV. The Measurement

(a) Calibration of the apparatus

The apparatus was calibrated by changing the temperature of the crystal in its mountings approximately 0.2° and measuring the corresponding deflection of the thermorelay galvanometer. The sensitivity of the apparatus can then be calculated since the expansion coefficient of the crystal and the temperature interval are known.

The coefficients of thermal expansion of Bi crystals were taken from the measurements of Ho and Goetz[18] and correction was made for the expansion of the frame.

The *Pt* thermometer measures the variation of the air temperature, with which the temperature of the crystal does not coincide until the elapse of a certain time interval. This was found to be at least one hour, a time much too long for maintaining constant conditions within the other parts of the apparatus due to unavoidable gradual distortions. In order to eliminate this uncertainty the calibration was accomplished by changing the current supplied to the heating coil at 6 to 10 minute intervals. The resulting temperature variation of the air is somewhat as shown in Fig. 5, where curve *A* shows the air temperature recorded against time. The temperature of the crystal, as reflected by the record of the thermorelay galvanometer, is shown by curve *B*. Although the temperature of the crystal lags behind the air-temperature the former is known at any of the peaks C_1, C_2, etc., since at the point where the temperature variation 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.

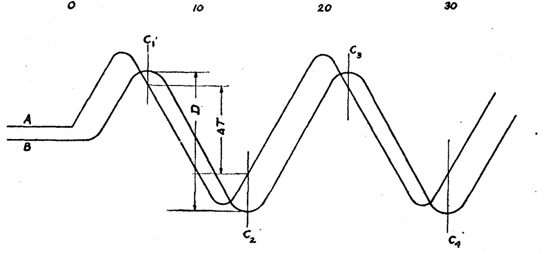

Fig. 5. Time-temperature diagram for the purpose of calibration. (*A*, air temperature measured by thermometer; *B*, crystal temperatures measured by thermorelay.)

If a drift occurs because of deformations of the apparatus, this can be recognized 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 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.

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 magnitostriction, particularly those made on short samples.

(b) Magnetostriction tests

The magnetostriction tests were carried out on a time-schedule, and Fig. 6 shows typical records of such measurements.

The marks at the top indicate the 15-second intervals. The time-axis runs from left to right. The line in the center is a record made by the thermorelay galvanometer. Deflections downward indicate an expansion of the crystal tested, deflections upward indicate contraction. The two sets of large deflections, extending almost across the records are the calibration of the lamp intensity, being checked just before and just after each test, because of the dependence of the total sensitivity on the light intensity. On the records shown in the figures these deflections were produced by a vertical displacement of the mi-

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[18] A. Goetz and R. C. Hergenrother, Phys. Rev. 40, 643 (1932).

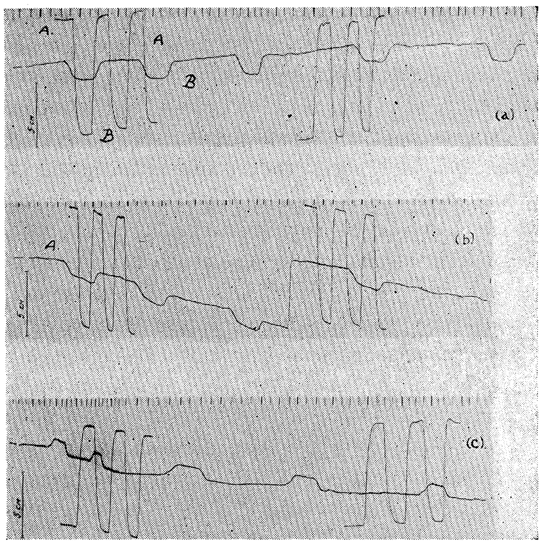

FIG. 6. Magnetostriction records. (The points A designate the moment, when the field current was started, the points B when the field was taken off. On the same record are the calibration curves of the intensity of the light source for the thermorelay, indicating also the temperature drift inside the dilatometer.)

crometer stage of the thermorelay of 0.056 mm.

The magnetostriction in Fig. 6a is an expansion, $(\Delta l/l)$ of 34×10^{-8}. This was the largest effect observed in any of the tests. Fig. 6b shows an expansion of 19×10^{-8}. Fig. 6c shows a contraction of 22.5×10^{-8}. A fairly rapid thermal expansion of the crystal can be seen in Fig. 6b. In order that the line should not drift off the paper, the thermorelay was displaced about the middle of the record.

Immediately after each test of the type described above a mirror was attached with wax to the face of the glass window (27, Fig. 3) in front of the rotating mirror (22, Fig. 3), and the identical procedure was gone through again. This is equivalent to conducting the test with the rotating mirror effectively locked. Any deflection of the thermorelay 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}.

(c) Discussion of errors

There are two chief sources of error, *viz,* (a) imperfections in the crystals and (b) observational errors.

(a) 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 except that the principal axis of the P_3 crystals was inclined about 4° from the axis of the rods instead of being parallel. Kapitza's[11] work shows that this introduced a negligible error of about 0.3 percent.

The amounts of impurities given for the alloyed crystals are the amounts added to the melt from which the crystal was grown. Previous experiments[15] indicate that in the P_1 crystals grown rapidly (6 mm per min.) the impurity is uniformly distributed. The P_3 crystals were grown more slowly (1 mm per min.) and 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.

(b) The observational error can be estimated as follows: An uncertainty of 1 percent in the coefficients of thermal expansion introduces a corresponding error in the calibration and accordingly in the final result.

The measurement of the magnetic field involved an error of about 2 percent, hence 4 percent in the magnetostriction. The error was of this magnitude since the coil gradually short circuited in the later part of the investigation and the field intensity was calculated by interpolation between successive calibrations.

A creeping motion of the galvanometer which attained an amplitude of about 1 mm (Fig. 6a–c) introduced an average error estimated at 5 percent with pure Bi crystals in a field of 26 kg. This background motion set the limit of magnification possible. The motion was reduced to about 1/3 by blowing a broad stream of air across the light path. Evidently a part of the creep was caused by temperature gradients causing irregular diffraction of the light beam.

The total error then is about 10 percent in measurements on pure Bi in a field of 26 kg. The error may be slightly larger when weaker fields or alloyed crystals are used.

The magnetostriction of the frame work was checked and was found unmeasurably small.

The elastic deformation of the crystal due to mechanical stress by its mountings was found to be only 2 percent of the magnetostrictive deformation. Since an identical strain is applied by the thermal dilatation during the calibration (see 3a) no correction is necessary.

The effect of the inhomogeneity of the field of the solenoid (l.b. Fig. 2) along the crystal can be compensated by taking the root-mean-square value, assuming the quadratic dependence of the magnetostrictive effect on the field.

The deformation caused by the ponderomotoric forces acting upon a diamagnetic substance in an inhomogeneous field can be neglected as it results in the worst case (direction of smallest modul and largest susceptibility) in an elongation of 0.15 percent of the magnetostriction. Since the crystal is mounted symmetrically to the solenoid a one-sided force is avoided.

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°C to about 50°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, as can be seen on the records (Fig. 6).

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. Since at least four tests are made on each crystal, no serious error should 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 corresponding elongation, however, is not over 0.01 percent of the total effect.

Finally the magneto-caloric effect (Langevin[19]) has to be considered, which depends upon the temperature coefficient of the susceptibility determined by Goetz and Focke.[15] In case of an ideally adiabatic process the effect would cause a thermal contraction of 0.5 percent of the total effect for P_3 and 1 percent for P_1. Since the real process is practically isothermal the actual error will be very much smaller and can be neglected.

V. Results

(a) Definition of the modulus of magnetostriction

The term "magnetostriction" as used throughout this paper designates only one of the several known phenomena of magnetostriction: the so-called Joule-effect. This is the change in the length of a long rod ($\Delta l/l$) when subjected to the action of a homogeneous longitudinal magnetic field.

The longitudinal stress p thus caused in the rod can then be expressed in terms of the field strength H, the susceptibility χ, Young's modulus Y and Poisson's ratio σ (χ, Y, σ with reference to the direction of p in an anisotropic substance) by:

$$p=-\int(Y\partial\chi/\partial p+\chi(1-2\sigma))HdH. \quad (1)$$

And since $\Delta l/l=p/Y$ and Y can be assumed to be invariant with H:

$$\Delta l/l=-\int(\partial\chi/\partial p+(\chi/Y)(1-2\sigma))HdH. \quad (2)$$

Since in case of a non-ferromagnetic substance $d\chi/dH=0$ at room temperature, $\partial\chi/\partial p$ is independent of H, and Eq. (2) reduces thus by integration to:

$$\begin{aligned}\Delta l/l&=-\tfrac{1}{2}H^2(\partial\chi/\partial p+\chi/Y(1-2\sigma))\\&=-\tfrac{1}{2}H^2m, \quad (3)\end{aligned}$$

where m shall be called the *modulus of magnetostriction*, since it is independent of H (if the invariance of Young's modulus with the field can be taken for granted). From experimental data the modulus of magnetostriction can thus be derived as:

$$m=2\Delta l/(l\cdot H^2). \quad (4)$$

The second term in Eq. (3) is negligibly small in case of Bi, since for a pure P_1-crystal $\chi/Y=1.05\times 10^{-6}\times 9.8\times 6.17\times 10^{-13}$,[15, 20] whereas σ is

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[19] P. Langevin, Ann. de chim. et phys. **5**, 123 (1905).

[20] P. W. Bridgman, Proc. Am. Acad. Sci. **60**, 305 (1925).

about 0.25, the total being smaller than 10^{-17}, whereas the experimental value of m is larger than 10^{-16}. Thus in our case the modulus of magnetostriction can be defined with an accuracy higher than the experimental error (i.e., <10 percent) as:

$$m = 2\Delta l/lH^2 = \partial\chi/\partial p. \tag{4a}$$

(b) 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).

TABLE I. *Longitudinal magnetostriction in Bi crystals.* (Pure Bi.) ($T = 25°$C.)

A, crystal orientation; B, designation of Bi; C, temperature coefficient of expansion; D, magnetic field; E, longitudinal magnetostriction; E, modulus of magnetostriction.

A	B	C ($\times 10^6$)	D (gauss)	E ($\Delta l/l \times 10^8$)	F ($m \times 10^{16}$)
P_1, 30°	*H*	11.6	13,700	− 5.	
			19,300	−10.	
			25,900	−22.5	−6.65
P_1, 0°	*H*	11.6	14,200	− 6.	
			20,100	−13.5	
			26,000	−24.5	−7.3
P_3	*H*	15.9	13,600	+ 6.5	
			20,500	+13.	
			26,000	+19.5	+5.7
P_1, 0°	*J*	11.6	25,750	−22.5	−6.8
P_3	*J*	15.9	12,350	+ 6.5	
			18,700	+11.	
			24,000	+16.	+5.65

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 (4a). 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 percent; the difference between the two P_1, (0°), crystals is 7 percent.

The modulus of the P_1, (30°), crystal is within the limits of experimental error the same as that of the P_1 (0°) crystals.

The accuracy of the present investigation is not sufficient to distinguish between the two azimuthal orientations. Hence no further tests were made on crystals of the P_1, (30°), orientation.

TABLE II. *Moduli of magnetostriction in pure Bi crystals.* ($T = 25°$, $H = 25$ kg.)

Crystal orientation	P_1, 0°	P.
Modulus "m"—this exp.	-7.05×10^{-16}	5.7×10^{-16}.
" " Kapitza	−7.3 "	6.5 "
Difference	3.5%	11.5%

Fig. 7 shows the magnetostriction values from Table I as function of the field strength; for comparison the values obtained by Kapitza[11] are added. Although the latter's work is not very accurate in the range of the smaller fields, there is good agreement. A comparison of the two investigations can also be made on the basis of the moduli of magnetostriction, as shown in Table II.

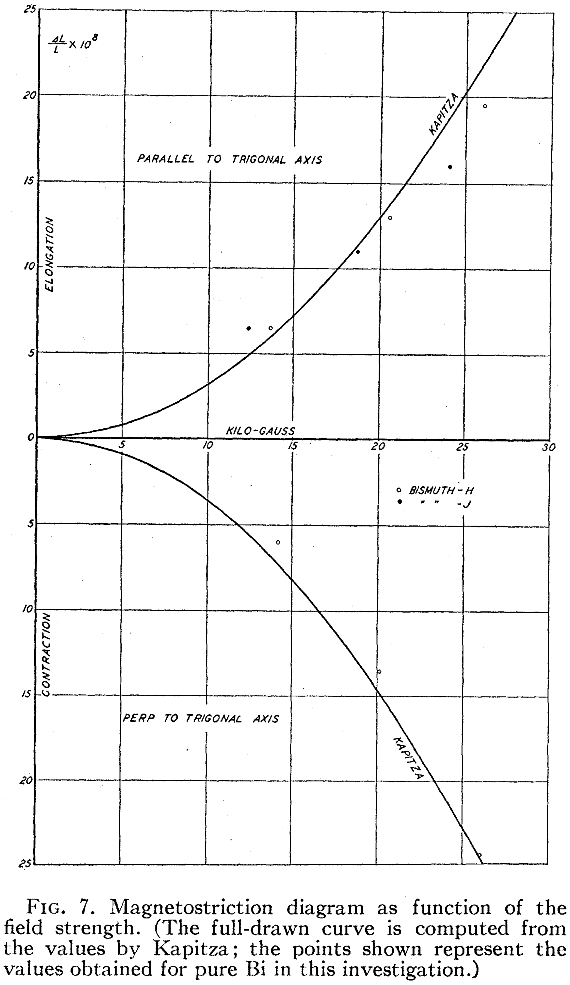

FIG. 7. Magnetostriction diagram as function of the field strength. (The full-drawn curve is computed from the values by Kapitza; the points shown represent the values obtained for pure Bi in this investigation.)

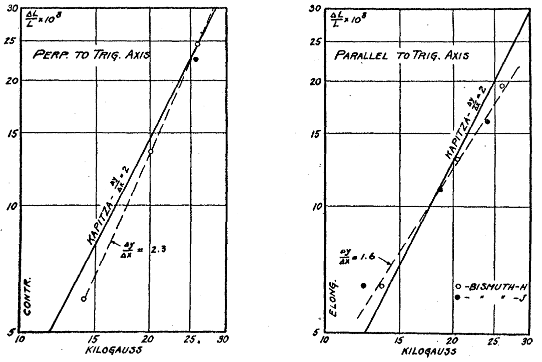

FIG. 8. Logarithmic magnetostriction diagram. (The full-drawn line represents Kapitza's H^2-dependence, the dashed line through the observed points indicates the closest straight line.)

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

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. 8. It is seen that the points lie practically on straight lines. From the inclination of the lines one obtains the equation:

$$\Delta l/l = k\cdot H^n. \qquad (5)$$

where $n=2.3$ for P_1 crystals (Fig. 8a), $n=1.6$ for P_3 (Fig. 8b) and $k=\text{const.}$ depending on crystal orientation. This appears to be valid between 15 and 25 kg.

Kapitza[11] obtained $n=2$ valid at least up to 100 kg. The present work, however, does not actually contradict Kapitza's, since the accuracy of both investigations drops so rapidly with decreasing magnetic fields that a definite determination of the exponent of H is not possible in weak fields.

(c) Magnetostriction in single crystals of alloyed 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 elements were selected on account of their mutual relations of valency configuration as discussed at length in a previous paper.[15]

The alloyed 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 right in Table III. The last column of the table gives the "percent 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 "percent magnetostriction" is plotted against the impurity in Fig. 9.

VI. DISCUSSION

The described results obtained for pure Bi crystals show that our values of the modulus of magnetostriction agree for field strengths between 20 and 25 kg with those obtained by Kapitza[11] as well as one could expect within the margin of experimental error. This agreement proves that his method of transient fields of very short duration is equivalent to the usual

TABLE III. *Longitudinal magnetostriction in bismuth single crystals. The effect of impurities.*

A, Crystal orientation; B, designation of Bi; C, type of impurity; D, amount of impurity;* E, temperature coefficient of expansion; F, magnetic field; G, longitudinal magnetostriction; H, modulus of magnetostriction; I, percent magnetostriction.**

A	B	C	D (% at)	E ($\times 10^6$)	F (gauss)	G $\left(\frac{\Delta L}{L}\times 10^8\right)$	H ($m\times 10^{16}$)	I (%)
P_1, 0°	*H*	—	—	11.6	26,000	−24.5	− 7.3	100
P_3	"	—	—	15.9	26,000	+19.5	+ 5.7	100
P_1, 0°	"	Te	0.3	11.6	25,750	− 6.5	− 1.9	26
"	"	Te	0.2	11.6	25,750	− 7	− 2.1	29
"	"	Te	0.1	11.6	25,750	− 9.5	− 2.9	40
"	*J*	—	—	11.6	25,750	−22.5	− 6.8	100
"	"	Te	0.05	11.6	25,750	−11	− 3.3	48
"	"	Sn	0.1	11.6	25,750	−17	− 5.1	75
"	"	Te	0.01	11.6	25,750	−19	− 5.7	83
"	"	Sn	2.5	12.5	25,750	+34	+10.3	−151
"	"	Sn	1.0	12.0	25,750	+19	+ 5.7	− 84
"	"	Sn	5.0	12.9	25,750	+33.5	+10.1	−149
"	"	Sn	0.5	11.6	25,750	+12	+ 3.6	− 53
P_3	"	Sn	0.9	15.0	25,750	+12	+ 3.6	64
"	"	Sn	4.4	14.7	25,750	+22	+ 6.6	119
"	"	Te	0.09	15.9	25,750	+15	+ 4.5	80
"	"	Te	0.24	15.9	25,750	+ 5	+ 1.5	27
"	"	Pb	1.0	16.4	24,000	+14.5	+ 5.1	90
"	"	—	—	15.9	24,000	+16	+ 5.55	100
"	"	Te	0.09	15.9	23,450	+10.5	+ 3.8	67
"	"	Sn	0.44	15.9	22,650	+12.5	+ 4.8	86
"	"	Sn	2.4	15.2	21,850	+13.5	+ 5.7	102
"	"	Pb	2.56	16.5	21,750	+14	+ 5.9	104
P_1, 0°	"	Pb	1.0	12.2	21,000	− 6	− 2.8	42
"	"	Pb	2.56	12.8	20,800	+ 5.5	+ 2.5	− 36
"	"	Pb	4.9	13.1	20,400	+15	+ 7.2	−105
P_3	"	Pb	4.9	16.7	20,400	+ 9	+ 4.3	78
"	"	Pb	2.56	16.5	20,400	+11.5	+ 5.5	99

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

** Modulus of magnetostriction expressed in percent of modulus for crystal of same orientation, but without the impurity.

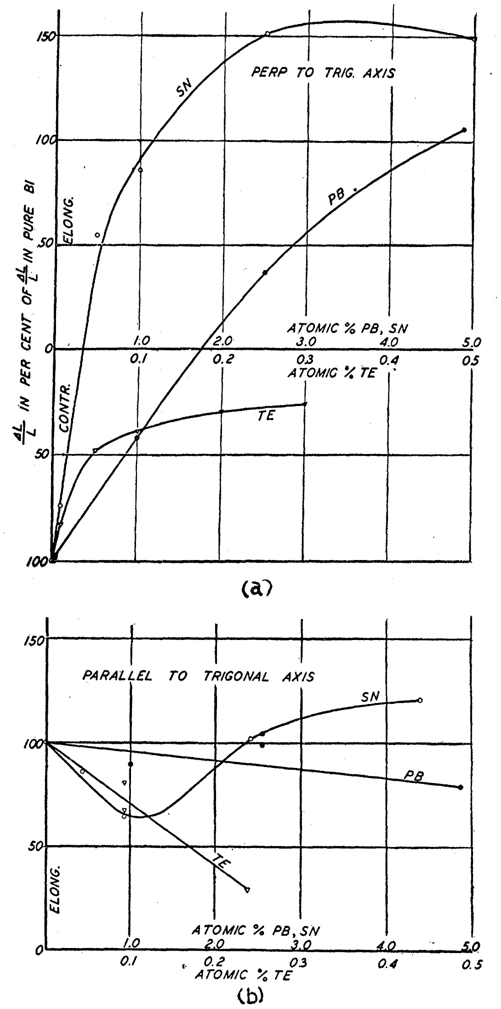

FIG. 9. Diagram showing the magnetostriction of alloyed Bi crystals relative (in percent) to the magnetostriction of pure Bi as function of the concentration of the admixture. Solid circle, *Pb*; circle, *Sn*; triangle, *Te*.

method of permanent fields under isothermal conditions, i.e., that the magnetostriction in a real crystal is an effect which does not involve a time lag larger than 10^{-2} sec.—a fact not necessarily anticipated in view of the structural differences between a real and an ideal crystal.

The only discrepancy between Kapitza's value and ours is the difference in the value of n in Eq. (5), consisting of a larger field dependence of the magnetostriction in the direction perpendicular to the trigonal axis and a smaller parallel to the axis than predicted by the simple thermodynamic theory. To what extent those deviations are real cannot be decided unless a better accuracy of the observations is obtained over a larger field range.

The main interest, however, lies in the results concerning the effect of foreign atoms upon the magnetostrictive qualities of the crystal, especially if they are compared with the effects upon the susceptibility as have been described in detail in a previous paper.[15] *

An examination of Fig. 9 will show that lead and tin exercise a particularly striking influence on magnetostriction *perpendicular* to the trigonal axis (P_1 crystals). About 0.4 percent of tin, or about 2 percent of lead reduced 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 effect of lead and tin on magnetostriction *parallel* to the trigonal axis (P_3 crystals) (Fig. 9b) is much smaller than in the case of P_1 crystals, and more complicated in character; thus no definite conclusion as to the ratio of the relative effects of the two admixtures can be reached.

The influence of the electronegative admixture Te is very much larger and different in character from that of Pb and Sn since no reversal in the sign of magnetostriction normal to the trigonal axis takes place.

A closer insight into the nature of these phenomena can be obtained by the following consideration: it has been shown before (*Va* Eq. (4)) that the modulus of magnetostriction is equivalent to a change in the susceptibility $(\partial\chi/\partial p)$ (longitudinal) under the elastic deformation produced by the stress (p). If one assumes in analogy to Kapitza's considerations that the application of stress and the change in the rela-

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* The great influence of admixtures in small concentrations was already observed by Kapitza when he replaced the pure Bi by a metal, the spectroscopic test of which showed traces of Pb and Ag; Kapitza mentions Kahlbaum as source of this metal which corresponds to our Bi "D", of which an analysis is given previously.[15] The admixtures have the tendency in both principal orientations to decrease the magnetostrictive effect. Our results conducted on a quantitative basis over a much larger range of concentrations confirm this observation.

tive positions of the atoms in the lattice thus caused, does not change the general character of the electron distribution within the lattice, one should expect the stress coefficient (ω') of the susceptibility to be proportional to the susceptibility itself. If the susceptibilities in a certain direction within the crystal without and with stress are χ_0 and χ_p:

$$\chi_p = \chi_0(1+\omega' p) \tag{6}$$

one obtains the relation:

$$m = \partial\chi/\partial p = \chi_0 \cdot \omega', \quad \text{and} \quad \omega' = m/\chi_0. \tag{7}$$

This consideration is applicable only if moduli of crystals are compared for which one has reason to assume a similar electron configuration. One such case is the comparison of the same crystals at different temperatures, as attempted by Kapitza;[11] another is the comparison of crystals at the same temperature containing admixtures in different concentrations within the region of solubility. This case seems to be of special interest, since the very large influence of admixtures upon the susceptibility of Bi crystals is known quantitatively.

Fig. 10 represents $\chi_\perp$ and $\chi_{||}$ as function of the (logarithmic) concentration of the admixtures used in this investigation for room temperature.*

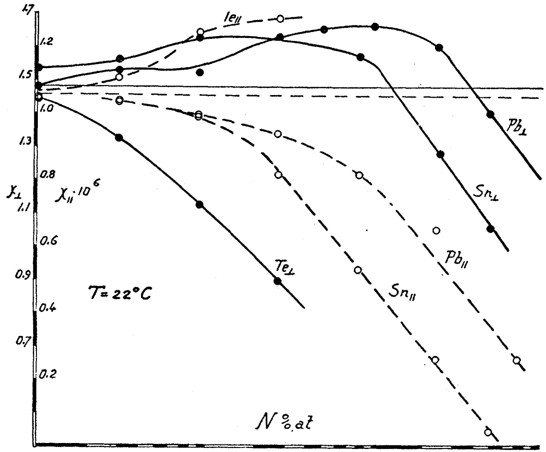

FIG. 10. $\chi(N)$ diagram for $T=22°\text{C}$.[15] The abscissa is on a logarithmic scale (0.01 percent at. to 10 percent at.); the ordinate has two scales: the left refers to $\chi_\perp$ (full drawn curves, solid circle), the right refers to $\chi_{||}$ (dashed curves, circle) respectively. The horizontal lines represent the values of $\chi_\perp$ and $\chi_{||}$ for pure crystals.

TABLE IV.

Metal	Orient	% at	χ (10^6)	χ_r	m (10^{16})	m_r	$m_r/\chi_r = \omega$
Bi	⊥	0.0	1.48	100	− 7.0	100	1.00
Bi+Te	⊥	0.01	1.48	99.8	− 5.7	83	0.835
"		0.05	1.23	83.2	− 3.3	48	0.577
"		0.1	1.12	75.5	− 2.9	40	0.53
"		0.2	0.96	65.0	− 2.1	29	0.45
"		0.3	0.87	59.0	− 1.9	26	0.442
Bi+Sn	⊥	0.1	1.66	112	− 5.1	75	0.67
"		0.5	1.60	108	+ 3.6	− 53	−0.49
"		1.0	1.55	104.5	+ 5.7	− 84	−0.80
"		2.5	1.28	86.5	+10.3	−151	−1.75
"		5.0	1.06	71.5	+10.1	−149	−2.08*
Bi+Pb	⊥	1.0	1.66	112	− 2.8	42	0.375
"		2.56	1.60	108	+ 2.5	− 36	−0.33
"		4.9	1.35	91.0	+ 7.2	−105	−1.15**
Bi	||	0.0	1.05	100	+ 5.7	100	1.00
Bi+Te	||	0.09	1.24	118	+ 3.8	67	.568
"		0.09	1.24	118	+ 4.5	80	0.677
"		0.24	1.26	120	+ 1.5	27	0.225
Bi+Sn	||	0.44	0.75	71.2	+ 4.8	86	1.20
"		0.9	0.50	47.5	+ 3.6	64	1.35
"		2.4	0.38	36	+ 5.7	102	2.84
"		4.4	0.08	24	+ 6.6	119	5.0*
Bi+Pb	||	1.0	0.97	86	+ 5.1	90	1.05
"		2.56	0.65	62	+ 5.5	99	1.6
"		4.9	0.36	34	+ 4.3	78	2.3**

* Interpolated from crystal (224/21$^{(15)}$).
** Extrapolated for 1.63% Sn$^{(15)}$ = 4.9% Pb.

If the suffix (p) refers to the pure crystal and the suffix (r) indicates the relative value, the following definitions can be chosen:

$$\chi_r = \chi/\chi_p; \quad m_r = m/m_p; \quad \omega = m_r/\chi_p;$$

$$\omega = \omega' \cdot \chi_p/m_p. \tag{9}$$

Table IV represents the numerical values of χ, χ_r, m, m_r, and ω, taken from Table III and from interpolations of Fig. 10. The functions $\omega_\perp(N)$ and $\omega_{||}(N)$ are given in Figs. 11a and 11b, respectively, in full drawn lines and solid circle, for comparison the values for $m_r(N)$ are added

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* The similarity in the effect of Pb and Sn is obvious, as is the difference of the effect in different orientations: for small concentrations ($<N_0$) $\chi_\perp$ is increased, for large concentrations ($>N_0$) it is decreased. The values of N_0 are: for Pb 3.75 percent (at.), for Sn 1.24 percent (at.), in quantative agreement to previous findings (Goetz and Focke) that the effect of Pb is one-third of that of Sn (since $N_{0\,\text{Pb}}/N_{0\,\text{Sn}} = 3.0_2$.

In contradistinction to $\chi_\perp$, $\chi_{||}$ is *only* decreased by Pb and Sn; for higher concentrations $d\chi/dN^{15}$ is the *same* in both orientations for Pb and Sn. This part of $\chi(N)$ can be described by:

$$\chi_{||} \sim \chi_\perp \sim \ln\,[N_0/N^b] \cdots (b=1.32) \tag{8}$$

where N_0 is the concentration for which $\chi_r = 100$ and $N \neq 0$.

The electronegative admixture Te increases $\chi_{||}$ and decreases $\chi_\perp$, i.e., it affects the crystal qualitatively in the opposite way than Sn and Pb.

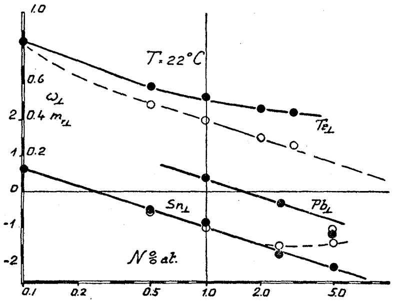

FIG. 11a. $\omega_\perp(N)$ diagram. The ordinate is on a linear scale; the left numbers refer to Pb and Sn, the right to Te. The abscissa is on a logarithmic scale (0.1 percent at. to 10 percent at.). For comparison the values of $m_{r\perp}(N)$ (Table IV) are added in dashed lines and circles. The numerical values of the ordinate have to be multiplied by 100 to obtain the values of $m_{r\perp}$.

in dashed lines and circle. For the direction normal to [111] the electropositive admixtures follow definitely a function of the form:

$$\omega_\perp = C - \delta \ln N = \ln [N_0/N^\delta] \qquad (10)$$

where δ is the same for Pb and Sn ($\delta = 1.4 \pm 0.3$) and N_0 equals 0.25 percent at. for Sn and 1.60 percent at. for Pb.

The analogy between $\chi_\perp(N)$ for higher concentrations (Eq. (8)) and $\omega_\perp(N)$ (Eq. 10)) is obvious; both functions are the same and within the limits of experimental error b equals δ. The differentiation of Eq. (8) and Eq. (10) results accordingly in:

$$d_\perp\chi/dN = -b/N; \quad d\omega_\perp/dN = -\delta/N;$$

$$dm_\perp/dN = -\chi_{0\perp}\cdot m_p\cdot \delta/\chi_p\cdot N \qquad (11)$$

$$\text{and} \qquad d\omega_\perp/d\chi_\perp = \delta/b = \text{const.} \sim 1. \qquad (11a)$$

Hence: *the change of the stress coefficient of the susceptibility with the concentration of foreign atoms is inversely proportional to the concentration;* furthermore: *the variation of the stress coefficient with the concentration is nearly equal to the variation of the susceptibility at higher concentrations*, or: *the stress coefficient of the susceptibility is proportional to the susceptibility itself.**

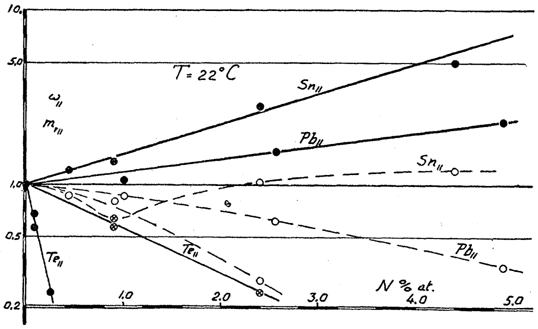

FIG. 11b. $\omega_{||}(N)$ diagram. The ordinate is on a logarithmic, the abscissa on a linear scale (0 percent to 5 percent at.). For comparison, the values of $m_{r||}(N)$ (Table IV) are added in dashed lines and circles. The numerical values of the ordinate have to be multiplied by 100 to obtain the values of $m_{r||}$. In order to show the linearity for Te, the values are plotted twice: once on the regular scale, solid circle, and once on a ten-fold N-scale, cross circle.

The comparison of $m_{r\perp}(N)$ and $\omega_\perp(N)$ in Fig. 11a shows that the function in Eq. (10) does not hold as well for the former as for the latter. (See footnote to page 1105.)

The validity of the function is limited to large concentrations of admixtures for $\chi_\perp(N)$ and probably also for $\omega_\perp(N)$ if measurements for sufficiently small concentrations were available. For $\chi_\perp(N)$ the relation ceases to be valid below 0.9 percent Sn and 2.7 percent Pb (Fig. 10), i.e., in the region where the admixtures cause an increase of the crystal diamagnetism in one direction ($\chi_\perp > 100$). It is interesting to note that the validity for $\chi_\perp(N)$ reaches much further—to the smallest concentrations measured (0.1 percent Sn and 1.0 percent Pb.) It is trivial that the relation in Eq. (12) holds only for concentrations where $\chi_\perp$ *and* $\omega_\perp$ follow Eq. (11).

In the direction parallel to [111] conditions are markedly different: it is seen from Fig. 11b that $\omega_{||}(N)$ is a simple exponential function. which can be written as:

$$\omega_{||} = \omega_{p||}(1 + N^{\delta'}) \qquad (13)$$

where $\delta' = 0.17$ for Sn; $\delta' = 0.072$ for Pb; and $\delta' = -3.4$ for Te ($\delta'_{\mathrm{Sn}}/\delta'_{\mathrm{Pb}} = 2.4$). Also here the comparison between $\omega_{||}(N)$ and $m_{r||}(N)$ shows that the simple exponential relation does definitely *not* hold for the former, e.g., the minimum .

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* This relation is proved quantitatively by the validity of:

$$\chi_1 + \omega_1\left[\frac{\chi_2 - \chi_1}{\omega_1 - \omega_2}\right] = C_{12} = \chi_2 + \omega_2\left[\frac{\chi_3 - \chi_2}{\omega_2 - \omega_3}\right] = C_{23}$$

$$= \chi_3 + \omega_3\left[\frac{\omega_1 - \omega_3}{\chi_3 - \chi_1}\right] = C_{31}, \text{ etc.} \qquad (12)$$

where χ and ω refer only to ⊥[111] and where the indices mean corresponding values of χ and ω (Table IV) for Pb *and* Sn. The variation among the values of C_{nm} thus obtained is ≤ 5 percent.

at $\mathrm{Sn}_{||}=0.9$ percent for $m_{r||}$ disappears for $\omega_{||}$.*

If there is a relation between $\chi_{||}(N)$ and $\omega_{||}(N)$ it is not a simple one. As is seen from Fig. 11 the $\chi_{||}(N)$ relation (Eq. (8)) holds for $N_{\mathrm{Sn}} \geq 0.3$ percent; $N_{\mathrm{Pb}} \geq 1$ percent (i.e., approximately one-third of the corresponding concentration of $\chi_{\perp}$), whereas $\omega_{||}(N)$ follows a simple function (Eq. (13)) for all concentrations.

The most marked result is the fact that the electropositive admixtures affect the crystal differently in different directions. The difference consists in the fact that parallel to [111] $\omega_{||}(N)$ is the same function beginning at the smallest concentration, whereas $\omega_{\perp}(N)$ shows a threshold for small concentrations $[\omega_{\perp}(N)]_{\mathrm{I}}$ and for large concentrations $[\omega_{\perp}(N)]_{\mathrm{II}}$. This can be interpreted that the disturbance of the electron configuration by the foreign atom is changed in character with increasing concentration.

Assuming the Ehrenfest-Raman[21, 22, 23] theory about the electron mechanism of crystal diamagnetism and the hypothesis by Goetz and Focke[15] concerning the process of electron scattering caused by foreign atoms dissolved in the lattice, the insertion of electropositive admixtures below the "critical concentration" follows approximately equidistant sets of planes with a large component parallel to [111], e.g., $(11\bar{1})$ or (110). Thus scattering walls in certain directions throughout the crystal are produced which affect the electromagnetic qualities accordingly. As long as N is small enough to saturate only such planes, only one direction in the crystal is affected. If, however, N is larger—so that the foreign atoms spread statistically over the whole volume of the crystal—the effect becomes similar in all directions.

The results of this investigation prove to be in good agreement with those conclusions, since the function of $\omega_{||}(N)$ for Pb and Sn is continuous, whereas there exist two forms for $\omega_{\perp}(N)$.* The validity of $[\omega_{\perp}(N)]_{\mathrm{I}}$ is thus restricted to the region of selective adsorption of foreign atoms, whereas $[\omega_{\perp}(N)]_{\mathrm{II}}$ holds for the region of volume absorption. At present our data for m are not sufficient to give a quantitative evaluation of $[\omega_{\perp}(N)]_{\mathrm{I}}$ except for the fact that $\delta > 0$.

The agreement with the electropositive admixture Te in the sense of this hypothesis is much less satisfactory, probably due to the incomensurability of the solution Bi+Sn (or Pb) and $\mathrm{Bi}+\mathrm{Bi_2Te_3}$.

Generally speaking, there are two handicaps which so far prevent a closer insight into the relation between crystal diamagnetism and magnetostriction: first, the absence of measurements of N at temperatures low enough to render the determination of N_c sufficiently exact; second, the indeterminacy of N in the solid crystal, about which subject a detailed investigation will be published soon from our laboratory.

Nevertheless, the present results support sufficiently the assumption that the effect of Sn and Pb in Bi in the region of selective adsorption ($<N_c$) is characterized by a disturbance of the electron configuration parallel to the principal axis, and in the region of volume absorption ($>N_c$) by a uniform disturbance which does not change any more the character of the electron lattice. Accordingly, the latter concentrations only show a proportionality between the coefficient of stress and the susceptibility. Thus the existence of the two types of insertion of foreign atoms in the crystal lattice seems to find another support.

In conclusion the authors wish to express their sincere obligation to Dr. W. S. Adams, Director of the Mt. Wilson Observatory and to Dr. A. S. King for the permission to use the solenoid, and their sincere thanks to Dr. A. B. Focke and Mr. J. H. Darlington for their help in preparing most of the crystals in this work.

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* The probability that this be caused by a faulty crystal is minimized by the fact that an entirely different set of crystals was used for the determination of $\chi_{||}(P_1)$ (Gouy method) and $m_{||}$ (P_3).

[21] P. Ehrenfest, Physica **5**, 388 (1925).

[22] P. Ehrenfest, Zeits. f. Physik **58**, 719 (1929).

[23] C. V. Raman, Nature **123**, 945; **124**, 412 (1929).

* For a detailed discussion of these directional relations reference is made to[15] Chapter 7.

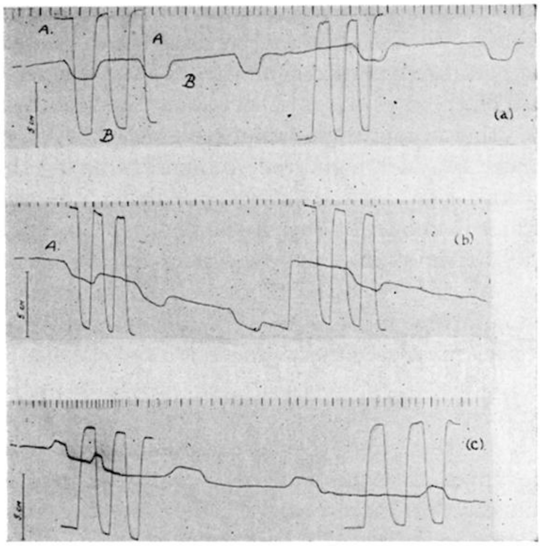

FIG. 6. Magnetostriction records. (The points A designate the moment, when the field current was started, the points B when the field was taken off. On the same record are the calibration curves of the intensity of the light source for the thermorelay, indicating also the temperature drift inside the dilatometer.)