

RESISTANCE CHANGE OF SINGLE CRYSTALS OF BISMUTH IN
A LONGITUDINAL MAGNETIC FIELD

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ABSTRACT

Resistance change of single crystal Bi as a function of magnetic field intensity.—Bismuth crystals of various orientations (angle between vertical crystallographic axis and length of specimen) show an increase in resistance in a magnetic field parallel to the specimen length. The fractional change in resistance $\Delta r/r$ is shown to be proportional to a power, slightly less than two, of the field intensity. In a maximum field of about 3500 gauss and at room temperature the increases in resistance range from 2 to 9 percent.

Resistance change of single crystal Bi as a function of orientation.—For a constant magnetic field (3480 gauss), the change in resistance when plotted against crystal orientation, shows maxima at orientations of 63° and 80° , and minima at 0° , 73° , and 90° . This effect is substantiated by observations on specimens whose orientations have been changed by grinding or splitting, since these show the same type of variation with orientation as do the separate crystals. To determine whether the effect is due to a lack of rotational symmetry about the vertical axis some experiments are described in which the position of the vertical axis was kept fixed and the position of a minor (digonal) axis varied slightly. No observable change was found.

Specific resistance.—The specific resistance, as a function of crystal orientation obeys the Voigt-Thomson symmetry relation. Comparison with recent results by Bridgman show a considerable difference, the explanation of which has presumably been given by Bridgman.

INTRODUCTION

OBSERVATIONS on the change in resistance of bismuth caused by a magnetic field have been made by many experimenters.¹ The effect in specimens composed of single crystals of bismuth has been measured by van Everdingen,² Lownds³ and Borelius and Lindh.⁴ In all these cases the crystal specimens were rods or plates sawed or cut from a large crystal in such a fashion as to have the desired orientation. No systematic investigation seems to have been made of the resistance change as a function of the orientation of the crystallographic axes with respect to the longest dimension of the specimen (for a rod or wire). The work reported here was undertaken with the purpose of making such a systematic study. It is confined, however, to the longitudinal effect, that is, to a study of the resistance change caused by a magnetic field which is in the direction of the length of the wire. The magnetic field and current in the specimen are thus parallel.

¹ See Campbell: Galvanomagnetic and Thermomagnetic Effects (1923) for bibliography.

² Van Everdingen, Phys. Zeits. **2**, 585 (1900-01).

³ Lownds, Phil. Mag. (6) **5**, 141 (1903) and Ann. d. Physik. (4) **9**, 677 (1902).

⁴ Borelius and Lindh, Ann. d. Physik (4) **53**, 97 (1917-18).

The bismuth crystal⁵ appears to belong to the trigonal system, ditrigonal-scalenohedral class, dihexagonal alternating type. It may be referred to rhombohedral axes, equal in length and mutually inclined at an angle of $87^{\circ} 34'$. The (111) plane is then the plane of easiest cleavage, is perpendicular to the trigonal, or vertical axis, and contains three digonal axes. A second cleavage which is apparently along a (11 $\bar{1}$) plane⁶ also exists. Rhombohedral cleavages were not observed in the specimens described below. In what follows the angle between the vertical axis and the length of the specimen is defined as the orientation. Positions of the digonal axes are not specified, since it was assumed at first that bismuth crystals have rotational symmetry about the vertical axis. For this and similar types of crystal, this assumption is certainly justified for many other properties, as has been shown by, or may be inferred from, the work of Bridgman,⁷ Grüneisen and Goens,⁸ Linder,⁹ Boydston,¹⁰ etc. This point will be discussed further below.

The crystals were prepared and orientations measured as described by Linder⁹ and Boydston.¹⁰ The bismuth used was the same as that used by Boydston.

DESCRIPTION OF APPARATUS

The magnetic field was produced by means of a solenoid made up of 155 turns of 0.8 cm copper tubing wound in five layers over a hollow cylindrical brass core. This core was 25.4 cm long, and 3.8 cm outside diameter. The constant for the solenoid was 7.33 gauss per ampere at the center and 7.15 gauss per ampere 5 cm either side of the central position, the average being 7.24. The solenoid was cooled by circulating water through the copper tubing. The water inlet was at the middle of the winding while the two ends of the solenoid served as outlets. Thus the water flowed from the center of the winding to both ends, producing efficient cooling. A General Electric 5 KW 10 volt generator was used to obtain the magnetizing current. This current was controlled by variation of the generator field by means of rheostats and a lamp bank.

The crystal was placed in a longitudinal groove in a wooden cylinder which fitted in the brass core of the solenoid. Two brass lugs were soldered to the ends of the crystal. They were allowed sliding room in case of any motion of crystal due to expansion or contraction. Flexible lead wires attached to the lugs were placed as nearly as possible on the axis of the solenoid. The wooden holder could be moved back and forth along the axis of the solenoid and was marked so that the same position was obtainable every time. The method of measuring the change in resistance was essentially a potentiometer method. A known current (about 0.3 amp.) was passed

⁵ Tutton, *Crystallography*, I, p. 138, p. 683; *Ogg. Phil Mag.* (6) **42**, 163 (1921); *James Phil. Mag.* (6) **42**, 193 (1921); *McKeehan, Jour. Frkl. Inst.* **195**, 59 (1923).

⁶ James, Ref. 5.

⁷ Bridgman, *Proc. Am. Acad. of Arts and Sci.* **60**, 305 (1925); **61**, 101 (1926).

⁸ Grüneisen and Goens, *Zeits. f. Physik* **37**, 378 (1926).

⁹ Linder, *Phys. Rev.* **29**, 554 (1927).

¹⁰ Boydston, *Phys. Rev.* (2) **30**, 911 (1928).

through the crystal and set up a potential difference between its ends. This potential difference was balanced in an auxiliary circuit. The value of a certain resistance, R , in this circuit with zero magnetic field was observed and this constituted a zero reading. With the field on R had to be increased to R' . The ratio, R'/R , is equal to the ratio $(r+\Delta r)/r$, where r is the crystal resistance and Δr is the increment in resistance. Computation of $\Delta r/r$ follows obviously. Zero readings were always taken both before and after the reading for any particular field. This was necessary as a drift in the zero always occurred when the field had been on for some time. This was undoubtedly caused by temperature change in the specimen.

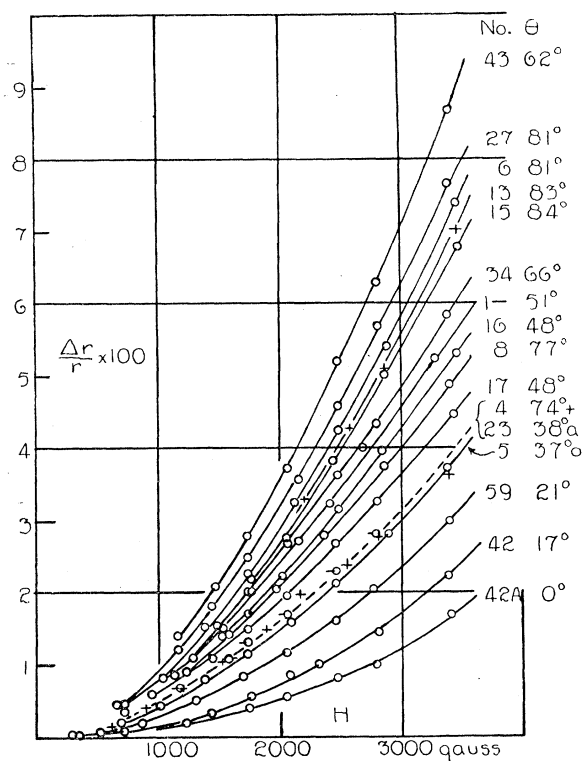


Fig. 1. Change in resistance as a function of the longitudinal magnetic field.

RESULTS

$\Delta r/r$ as a function of the orientation. About one hundred crystals were made with an orientation varying from 17° to 90° , and of these sixty-two were used. While in general it was possible to make crystals of most of the desired orientations by growing from a single parent crystal placed in the melt at the appropriate angle, difficulty was experienced in producing those with very low orientations.

Fifteen of the crystals were measured for nine different values of H up to 3480 gauss, and readings were taken on the rest for three or four field

strengths. The results for these fifteen are shown graphically in Fig. 1. It seems likely from various theories of galvano-magnetic effects that $\Delta r/r$ should be a parabolic function of the field strength. This has been found to be approximately true by other investigators and is found to be roughly true for all orientations in the present work.

Assuming the relation:

$$\Delta r/r = AH^z \quad (1)$$

where A and z are constants, a plot between $\log \Delta r/r$ and $\log H$ should yield a straight line whose slope is the constant, z . All the curves of Fig. 1 have been plotted to such a logarithmic scale and the points do fall upon straight lines, at least for field strengths above 1000 gauss. For lower fields some of the lines show an appreciable curvature, the slope increasing with decreasing H . The values of z obtained from the straight line portions of the curves are shown in Table I. With three exceptions, they are all notably

TABLE I
Values of z in the relation $\Delta r/r = AH^z$

Crystal No.	Orientation (degrees)	z	Crystal No.	Orientation (degrees)	z
42B	0	2.10	43	62	1.71
42	17	2.24	34	66	1.75
59	21	1.94	4	74	1.57
5	37	1.83	8	77	1.62
23	38	1.57	27	81	1.72
16	48	1.64	6	81	1.82
17	48	1.59	13	83	1.78
1	51	1.75	15	84	1.78

under 2, but there seems to be no consistent variation with orientation angle or magnitude of resistance change, except perhaps for the three lowest orientations. These are likewise the orientations which show the smallest change in resistance.

It can be seen from curves in Fig. 1 that the magnitude of the resistance change, for any field, does not increase continually with increasing orientation, since in many cases curves of higher orientation are below those of lower orientations. What seems at first to be mere inconsistency turns out to be a remarkably critical variation of the effect with orientation. This relationship is depicted in the curve of Fig. 2(a), in which are plotted observations at 3480 gauss on all the 62 crystals. While it is true that the points are scattered to an extent presumably beyond the probable error of the observations it seems likely that the general trend gives maxima at approximately 62° and 80° , and minima at 0° , 73° , and 90° . It must be remembered that the different points represent entirely independent observations taken on different crystals with many different parent crystals.

It is realized, of course, that the curve as drawn beyond about $\theta = 50^\circ$ needs considerable defense. There are only three points to establish the maximum at $\theta = 62^\circ$. However, if the observed values of these three points

are really as much as 0.02 too high, which is about the largest difference in $\Delta r/r$ values observed for any crystals of the same orientation, the maximum at 62° would still exist, though it would not be as pronounced as it is shown. Of the points between 70° and 74° , three are far above the curve, but there seem to be enough low points in this region to justify the curve as drawn. The maximum at 80° is considered to be established by the five high points at 80° - 81° , with no low points exactly at this orientation and only one neighboring high point ($\theta = 76^\circ$, $\Delta r/r = 0.078$) with about the same value of $\Delta r/r$. From 85° - 90° the points are very much scattered, but there is no doubt that the average value of $\Delta r/r$ for them is less than the corresponding quantity for the interval $\theta = 79^\circ$ - 82° . It may be said that it is not believed

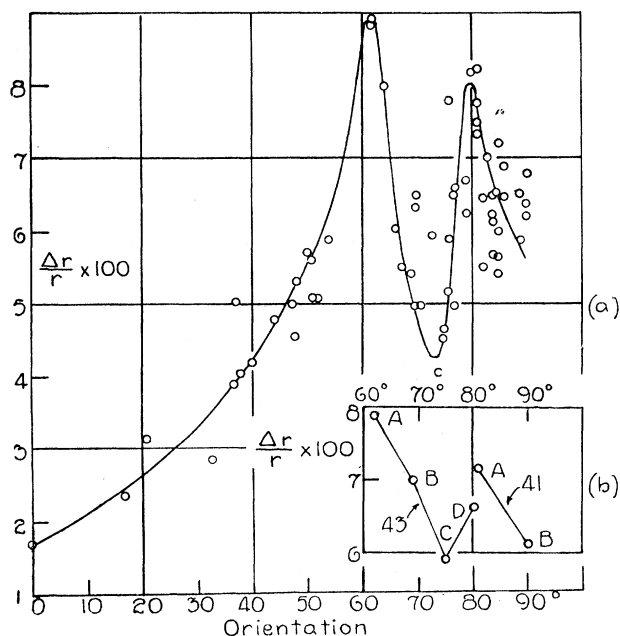


Fig. 2. Change in resistance as a function of orientation for a constant field: (a) Crystals measured as grown, $H = 3480$ gauss; (b) Modified crystals, $H = 3330$ gauss.

that the scattering is due to experimental error, although the angle measurement is accurate to only about 1° , which, of course, is rather serious in the neighborhood of a sharp maximum or minimum. The measurement of $\Delta r/r$ is believed to be accurate to one percent of the plotted values, since crystals could be taken out of the holder, resoldered and remeasured with results differing only by that amount. It may be mentioned also that both van Everdingen and Borelius and Lindh report values of $\Delta r/r$ for some intermediate orientations (60° and 45° , respectively), which are higher than the $\Delta r/r$ values for 0° and 90° . This gives some confirmation of the first maximum ($\theta = 63^\circ$). The writer has found no data for the longitudinal effect in the neighborhood of $\theta = 80^\circ$.

Of course, the curve of Fig. 2 will be repeated (as a mirror image) if the angle of orientation is extended above 90° , in which case the minimum at 90° appears even more striking, falling as it does between two maxima about 20° apart, quite similar to the minimum at 73° between the nearby maxima. A great deal of effort was given to establishing the reality of the minimum at 90° , as can be seen by the density of points above 80° . Orientations above 85° could not be measured on the spectrometer but were estimated.

The existence of maximum and minimum values for $\Delta r/r$ between $\theta = 0^\circ$ and $\theta = 90^\circ$ was so remarkable that it seemed desirable to have an independent check of it. Many variations can conceivably exist between apparently similar crystals made from the same melt due to slight differences in circumstances during growth, differences in handling, etc. It was, therefore, deemed advisable to measure the value of $\Delta r/r$ for the same specimen with direction of current flow in it and magnetic field in a different direction relative to the vertical axis. Within a narrow range this can be done. While it is not feasible to set up an appreciably non-axial current in a wire, it is possible to alter the axis of the wire by cutting or grinding from the surface, and so, in the case of the thicker crystals, to alter the relation between the principal axis and the direction of current flow by 10 or 15° . This experiment was actually tried. Crystal No. 41 was a thick one with an orientation of about 82° . It was measured and then split as carefully as possible along the main cleavage planes, giving a crystal with an orientation of 90° . When it was subsequently tested the value of $\Delta r/r$ was found to have decreased. This effect is shown in Fig. 2(b). For other variations in orientation it was necessary to grind instead of split the crystal. Several of the thicker crystals were treated in this manner and the results for one of them are also shown in Fig. 2(b). In this case (No. 43), the same crystal was changed in orientation by almost 20° , starting from 62° , corresponding to a large value of $\Delta r/r$. As the angle of orientation was increased, the value of $\Delta r/r$ at first decreased and later (as the angle approached 80°) increased, roughly paralleling the course of the curve of Fig. 2(a). The field used here was about 150 gauss lower than for the observations of Fig. 2(a).

Previous to this it had not been possible to make crystals of very low orientation. However, crystal No. 42 at 17° orientation happened to be a thick one and it was cut until the orientation was reduced to 0° and measured to give curve 42A in Fig. 1 and the point of zero orientation in Fig. 2(a).

Although, in the above, strains were avoided as much as possible, it was desirable to see what effect strains would have on $\Delta r/r$. To test this point several crystals were severely bent while in the holder and then remeasured. There was very little difference between the readings before and after bending.

An experiment which may throw a little more light on the significance of the results shown in Fig. 2 consisted in altering slightly the direction of the magnetic field with respect to the wire axis, to see whether the values of $\Delta r/r$ found were primarily functions of the relative orientation of the magnetic field and the crystal or of the electric field (*i.e.*, the current) and

the crystal. While of course the effect might differ very much if the magnetic field is changed from a longitudinal to a transverse direction it was thought possible that a significant change might be detected with only a small change in the field direction when working on the crystal near a critical orientation. No such changes were observed, however, with changes in the direction of the field as high as 10° . This rules out the hypothesis that the relation of the magnetic field to the crystal axis is primarily responsible for the observed effect. Even with a picture of a more or less isotropic current distribution in the absence of a magnetic field (*i.e.*, with motions of electrons in substantially all directions with the velocity of thermal equilibrium except for the drift produced by the electric field), it might still be supposed that the magnetic field could have the effect found if we supposed that at some orientations

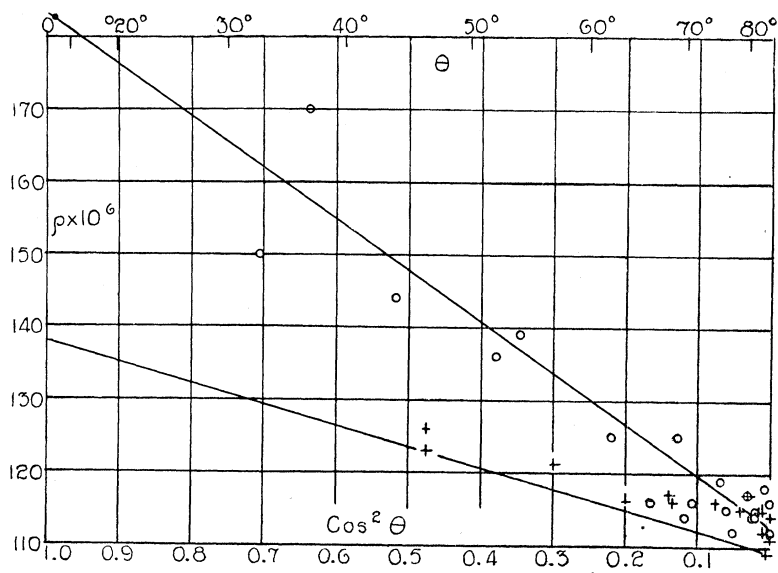


Fig. 3. Specific resistance, plotted to test Voigt-Thomson symmetry relation. The crosses represent the observations of Bridgman, the circles those of the writer.

it was able to direct electrons into atoms which would terminate their free paths and for other orientations would enable the electrons to escape those obstacles. The experiment described above seems to rule out this hypothesis.

As a further check, it was considered desirable to find out whether an effect similar to that found for $\Delta r/r$ existed in the value of the resistance itself, *i.e.*, whether the critical effect was due to the numerator or denominator of $\Delta r/r$. As the crystals were not uniform in cross section an average cross section was found by weighing and dividing by the product of the density and the length of the sample. Knowing the drop in potential across a crystal and the current through it the specific resistances could then be calculated. Naturally very accurate results cannot be obtained with these non-uniform crystals. The specific resistance, ρ , should satisfy the Voigt-Thomson sym-

metry relation. This is tested, as usual, by plotting values of ρ against $\cos^2\theta$, where θ is the orientation. Fig. 3 shows such a plot, the writer's observations being indicated by circles while observations by Bridgman¹¹ are indicated by crosses. In both cases a straight line may be drawn through the points though not the same line. In particular, the value of specific resistance for $\theta=0$ is quite different, Bridgman's value being considerably lower. The line for Bridgman's observations has been drawn through what he considers the most probable values of ρ_{\perp} and ρ_{\parallel} . Although the writer's results agree with earlier observations, as shown in Table II, it must be stated that Bridgman attributes the high resistance for $\theta=0$ to the existence

TABLE II
Specific resistances of the two principal orientations.

Observer	$\rho_{\parallel} \times 10^6$	$\rho_{\perp} \times 10^6$ (ohms/cm ²)	$\rho_{\parallel}/\rho_{\perp}$
Matteuci	—	—	1.60
van Everdingen	348	207	1.68
Borelius and Lindh	192	124	1.55
Bridgman	138	109	1.26
Writer	183	113	1.62

of fissures parallel to the main cleavage plane. Borelius and Lindh (ref. 4, p. 124) note also that a specimen of zero orientation has its resistance lowered by compression in the direction of the vertical axis. It is possible that the method used by the writer to prepare his crystals might produce such minute fissures since the upper portion of the crystal during growth is strained by the weight of the part below it. It must be noted, however, that this effect, if it exists, apparently does not invalidate the linear relation between ρ and $\cos^2\theta$. Further, disturbing effects would be least for crystals of high orientation (60° – 90°) and it is in this region that the maxima and minima of Fig. 2 occur. It is concluded that there is no critical variation of resistance with orientation which would account for the relation between $\Delta r/r$ and orientation.

In this investigation, as stated before, the resistance change has been considered as a function of only a single variable, the orientation of the vertical axis. To define exactly the crystal position one other angle coordinate is necessary, such as the direction of one of the digonal axes with respect to the specimen axis. Hitherto it has been found that galvanometric effects (such as those following the Voigt-Thomson law) depend only on the position of the principal axis, but with a phenomenon so sensitive to angle change as the present one, it seemed likely that the direction of one of the digonal axes could not be neglected. For instance, when the principal cleavage planes are across the wire (zero orientation) a minimum effect is found; it might well be that where the minor cleavage plane ($11\bar{1}$) is exactly across the wire axis that another minimum should occur, and in fact this might well account for the minimum at about 73° orientation since the angle between these two

¹¹ Bridgman, Proc. Am. Acad. of Arts and Sciences 60, 351–2 (1925).

planes has about that value. Variations in orientation of a digonal axis might also account for the scattering of the points. Consequently the experiment was tried of keeping the principal orientation fixed and varying the orientation of a minor axis (digonal) as shown by the relative position of the secondary $(11\bar{1})$ cleavage planes. Crystals could be made by suitably adjusting the angle of contact of the parent crystal before raising from the melt so that the principal cleavage planes in each case were approximately parallel while the minor cleavage plane could in successive crystals be shifted so that it made different angles with the wire axis. No change could be detected however in the value of $\Delta r/r$ which could be attributed to this change. In particular, crystals with minor cleavage planes cut exactly across the crystals¹² did not show an extremum when compared with other crystals of the same principal orientation but different minor orientations. The experiments along this line were not very extended, however, as they are somewhat difficult to control. The principal orientation, upon which the effect depends so sensitively, is especially difficult to produce exactly as desired and to measure accurately. Apparently similar crystals did not always give identical results. Moreover the range of variation in orientation of the $(11\bar{1})$ planes which could be produced was not very large. Possibly the effect of this minor orientation could be found by using a single large crystal cut into different forms.

Before the complexity of the phenomena presented at room temperature was understood, measurements were made on some of the crystals at liquid air temperatures. This work must be more thoroughly done before it can be reported upon, but it may be said that the results at low temperatures do not follow the same laws as at room temperature. This is not surprising since the effect at these low temperatures is of the order of 20 times greater than the effect at room temperature. A theory of the effect which would apply when Δr is small compared with the resistance itself will involve approximations which cannot possibly be valid when the resistance change is comparable to the initial resistance.

In conclusion the writer wishes to express his indebtedness to Professor E. P. T. Tyndall, who suggested the problem and under whose direction the work was mainly done, and to Professor J. A. Eldridge, for their ever-ready assistance and inspiration.

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¹² In general, crystals of high orientation seem most inclined to grow with the minor cleavage plane almost perpendicular to the wire axis.