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The electrical resistivity of gallium and some other anisotropic properties of this metal

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It is shown that single crystals of gallium can be produced with considerable ease, and that these crystals show greater anisotropism in their conducting properties than those of other metals. At normal temperatures the electrical conductivities for the three axial directions $c:a:b$ are in the ratio 1:3·2:7, and the expansion coefficients are in the ratio 1:0·7:1·9. Results are given showing that these ratios persist down to −180° C with relatively little change. From preliminary observations at normal temperature it seems that the thermal conductivity varies much as does the electrical conductivity and that the mechanical properties will also prove to be markedly anisotropic.

Introduction

Until recently the metal gallium has been available in only small quantities, yet several workers have made determinations of its electrical resistivity. Guntz & Broniewski (1908) for the solid metal obtained values of 53·4, 56·5, 57·0 and 55·8 microhm cm. units for the specific resistance at temperatures of 0, 17·4, 18·6 and 26·4° C respectively and for the liquid metal values of 28·4, 27·2 and 28·0 microhm cm. units at temperatures of 46·1, 30·3 and 18·6° C. This last determination was made on the super-cooled liquid, since the normal melting-point is 29·8° C. Bridgman (1921*a*) failed to find either the maximum in the resistivity for the solid phase or the minimum for the liquid phase. For the super-cooled liquid he stated that the resistivity at 0° C gave a point on a regular prolongation of the curve for the resistivity above the melting-point. From the information contained in Bridgman's paper the following values can be deduced: for the solid, 40·15 at 0° C and 44·9 at the melting-point; for the liquid 25·92, 26·7 and 27·4 microhm cm. at 30, 65 and 100 °C respectively. He considered that gallium behaved abnormally and resembled antimony and bismuth in that the resistance of the solid metal at the melting-point was 1·733 times that of the liquid but behaved normally in that increase of pressure resulted in a decrease in resistance.

de Haas & Voogd (1929) showed that gallium became superconducting at a temperature of 1·07° K. No values, however, were quoted for the specific resistance of the metal in this paper nor in a later paper by de Haas & Voogd (1931) which expresses the resistance over the range from liquid-oxygen to liquid-helium temperatures as a proportion of the resistance at 0° C. Kapitza (1929) and de Haas & Blom (1933–4, 1937*a, b*) have studied the effect of magnetic fields on the resistivity of single crystals of gallium, but here again most of these results are expressed as proportional changes. de Haas & Blom (1937*a*) do make just one mention of the specific resistance of the single crystals of gallium they had studied, which were stated to have been grown in directions parallel to the three crystallographic axes of this orthorhombic metal. They say 'From the proportions of the crystals the specific resistance at 0° C for the three crystals has been calculated. As the wires were very small, no great accuracy could be reached. Within the errors of measurement the same value for the three crystals was found:

$$\rho_0 = 52{\cdot}7 \times 10^{-6}\,\Omega\text{cm.'}$$

The foregoing account summarizes the data available for the electrical resistivity of gallium in January 1949 when the present author obtained a sample of gallium which had been prepared by the Chemical Research Laboratory. It will be seen that these measurements had given no indication of the high degree of anisotropy which immediately became apparent and which has been referred to in two preliminary publications (Powell 1949, 1950). The present account deals with these anisotropic properties in greater detail and gives electrical resistivity and linear expansion data for crystals grown in the three axial directions down to liquid-oxygen temperatures. Further resistivity measurements to lower temperatures made at the Clarendon Laboratory, Oxford are being described in a separate publication (Olsen-Bär & Powell 1951).

Preliminary measurements on gallium specimens supplied by the Chemical Research Laboratory

The gallium used for the initial measurements had been extracted from flue dust deposits by means of a method described by Reynolds (1950). The metal was stated to be of high purity. Spectroscopic analysis carried out on the oxide, derived from the metal by the action of nitric acid has indicated the results tabulated below.

element	present in parts per million	element	present in parts per million
aluminium	20 to 30	antimony	< 10
arsenic	< 3	silicon	30
chromium	< 1	tin	< 1
iron	10	vanadium	1 to 2
germanium	5	zinc	4
lead	1		

It was considered possible that the relatively large amounts of common constituents such as aluminium and silicon present in the oxide are derived from the nitric acid. On the other hand, results for uncommon constituents like germanium, antimony and zinc, are probably representative of the metal itself. The 'less than' sign implies that the metal was not detected, and that the sensitivity of the method for that particular element was the value quoted. Accepting the results for the oxide, the purity of the metal will be better than 99·99 %.

Figure 1 contains all the information available for the electrical resistivity of gallium at the time the present investigation was commenced on the samples supplied by the Chemical Research Laboratory and also the results obtained for the earliest of these samples. No special precautions had been taken when casting these rods, and it will be observed that the values obtained for the nine rods ranged from 9 to 51·3 microhm cm. For sample no. 9 the two ends of the rod gave values of 40·8 and 19·3 respectively.

The conclusion was reached that this range of resistivity values could be explained by the existence of varying preferred orientations in the different specimens. In the case of sample no. 9 the crystal growth had probably started from two sources. After some of the gallium specimens had been tested over a wider range of temperatures (see figure 1), the experiments were directed towards determining the manner in which the electrical resistivity of gallium varied with the orientation of the crystal.

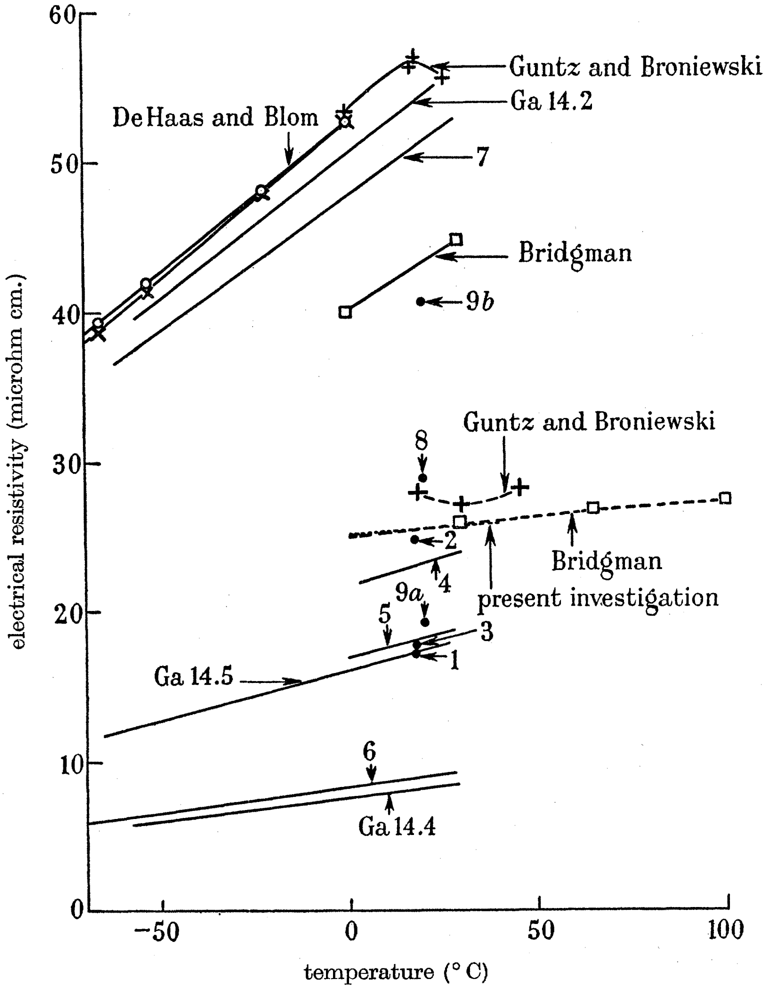

FIGURE 1. Electrical resistivity of solid and liquid gallium. Numbers 1–9 relate to first gallium samples included in present investigation. Numbers 14·2, 14·4 and 14·5 approximate to the three axial directions. Liquid gallium shown by dotted lines

Experiments directed towards determining the dependence of electrical resistivity on crystal orientation

Specimen Ga 11

By way of a preliminary experiment two open ended glass tubes were fused to a length of glass tubing at distances of 7 and 11·5 cm. from one end so as to be perpendicular to the main tube and to each other. All the tubes had a diameter of about 4 mm. Liquid gallium was drawn up into the tube and prevented from running out again by sealing the bottom and side tubes with glass plugs attached by rubber tubing. The gallium had been freshly cleaned with dilute acid and several small bubbles adhered to the walls of the tubing. The tubing was supported in a beaker of water at 27° C, the main stem being vertical and the gallium surface just exposed.

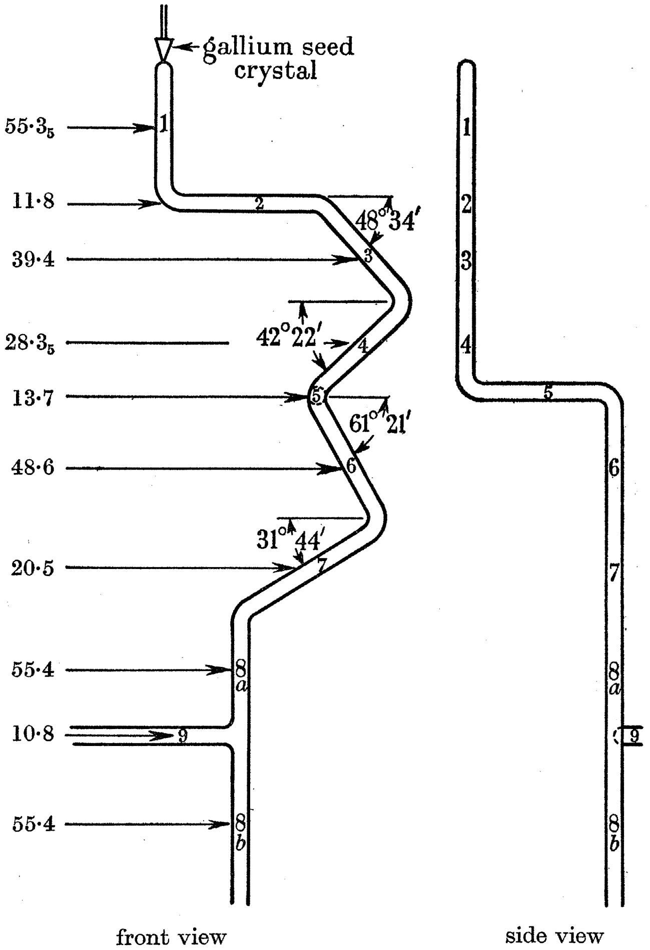

FIGURE 2. Sketch of specimen Ga 12 grown in bent glass tubing and showing electrical resistivity (microhm cm.) of each section at 17° C.

Crystallization was started by introducing the sharp point of a small pyramidal crystal of gallium into the liquid, the crystal being supported with the geometrical axis through this well-defined point approximately in line with the main stem of the tubing. The progress of the crystallization could be readily followed, as the solidified metal was darker in appearance. After the solidification was complete the glass was removed by careful filing and crushing with pliers, and the specific resistances of various sections of the metal were measured. These values are only approximate, owing to the uneven nature of the surface due to the bubbles which had adhered to the glass and are likely to err on the high side as they are based on diameter measurements made with a micrometer. The resistivities determined for the three sections of the main stem were 55·2, 55·0 and 54·7 microhm cm. and those for the two side arms were 13·5 and 14·0 microhm cm. This result again suggests that the gallium had grown as a single crystal and that the electrical resistivity varies considerably for different directions within the crystal. That the branched specimen was a single crystal was further tested by etching for a short time in dilute hydrochloric acid. This treatment exposed brightly reflecting crystal faces which were seen to be alined in the same direction over the whole surface of the specimen.

Specimen Ga 12

The next experiment tried was to solidify the gallium in a length of glass tubing previously bent to comprise several different directions. The tubing had an internal diameter of 0·44 cm. and its form is indicated in figure 2. The sections marked 1, 2, 3 and 4 were bent in the plane of the paper at the angles shown, section 5 was normal to this plane and sections 6, 7, 8*a* and 8*b* were again in the plane of the paper, the last two coinciding with the direction of the first section. The side arm (section 9) served as an expansion chamber during the solidification of the metal. It had not been intended for observation and was located in a plane at a small unnoted angle to the plane of the paper. This time the tube was filled with clean dry gallium and solidification was carried out just as before. The absence of moisture in the tube resulted in so close a contact between the glass and solidified metal that it no longer proved possible to remove all the glass from the metal. In order to enable the room temperature resistivity determinations to be carried out, two V-slots were ground in each section at spacings of about 3 cm., care being taken not to dissipate sufficient heat to cause melting and to discontinue grinding as soon as the metal was reached. Copper wires to serve as potential leads were then 'welded' into the gallium at the base of each slot by momentarily touching them with the head of a heated pin. The values obtained at 17° C for the electrical resistivities of this specimen, referred to as no. 12, are indicated in figure 2 and are set out in table 1.

TABLE 1. ELECTRICAL RESISTIVITY DATA AT 17° C FOR VARIOUS SECTIONS OF SPECIMEN GA 12

(ϕ = angle between first and other sections in same plane.)

section no.	ϕ	$\sin\phi$	$\sin^2\phi$	electrical resistivity (microhm cm.)
12·1	0	0	0	$55{\cdot}3_5$
12·2	90	1·0	1.0	11·8
12·3	138° 34′	0·6617	0·438	39·4
12·4	227° 38′	−0·7389	0·546	$28{\cdot}3_5$
12·5	in plane perpendicular to other sections			13·7
12·6	151° 21′	0·4795	0·230	48·6
12·7	238° 16′	−0·8505	0·724	20·5
12·8 (*a* and *b*)	0	0	0	55·4

The close agreement between the resistivity values for the first and last sections implies that the crystal orientation had remained constant during the solidification and was unaffected by the directional changes imposed by the glass tubing. Thus the resistivity values obtained for all the sections located in one and the same plane should conform to the ellipse which represents the intersection of that plane with the conductivity ellipsoid—the ellipsoid for which the square of the radius vector is equal to the electrical conductivity.

If $2a$ and $2b$ be the major and minor axes of this ellipse and ρ_ϕ be the resistivity in a direction at an angle ϕ to the major axis then,

$$\rho_\phi = \rho_a \cos^2\phi + \rho_b \sin^2\phi, \tag{1}$$

where

$$\rho_a = 1/a^2 \quad \text{and} \quad \rho_b = 1/b^2;$$

thus

$$\rho_\phi = (\rho_b - \rho_a)\sin^2\phi + \rho_a, \tag{2}$$

which indicates that a straight line should result when ρ_ϕ is plotted against $\sin^2\phi$. Figure 3 shows the data of table 1 plotted in this way. The ringed points obtained, on the assumption that the direction of section 12·1 coincides with the major axis of the ellipse, do not conform to a straight line. The straight line

$$\rho_\theta = (11{\cdot}6 - 55{\cdot}7)\sin^2\theta + 55{\cdot}7 \tag{3}$$

does, however, result for an angle $\theta = \phi + 4° 30'$, suggesting that the major and minor axes of the ellipse are inclined at angles of 4° 30′ and 85° 30′ to the direction of section 12·1. Referred to these axes the equation of this ellipse is

$$55{\cdot}7x^2 + 11{\cdot}5y^2 = 1. \tag{4}$$

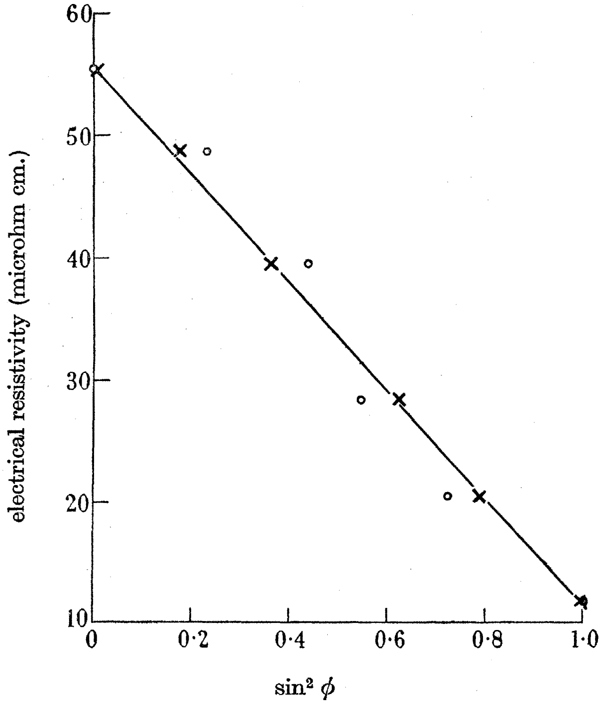

FIGURE 3. Specimen Ga 12; variation of electrical resistivity with $\sin^2\phi$. ○ Axis assumed to coincide with direction of Ga 12·1. × Axis assumed at 4° 30′ to direction of Ga 12·1 (ϕ increased by 4° 30′).

The fact that the resistivity of section 12·5, in a direction normal to the plane of this ellipse, differed from either of the present axial values indicates that the conductivity ellipsoid of the gallium crystal is not an ellipsoid of revolution and that for the determination of this ellipsoid at least three resistivity measurements made in each of the three mutually perpendicular planes will be necessary.

In passing, it might be observed that specimen Ga 11 gave one set of values for these orthogonal directions and specimen Ga 12 gave three further sets (sections 1, 2 and 5, 3, 4 and 5 and 6, 7 and 5). The sum of the observed resistivities for these four sets are 82·5, $80{\cdot}8_5$, $81{\cdot}4_5$ and 82·8 microhm cm. respectively and are seen to be approximately constant.

Electrical resistivity of molten gallium

At this stage of the investigation a length of glass tubing bent to comprise twelve sections giving four directions in each of three mutually perpendicular planes was prepared. Potential leads consisting of fine platinum wires were fused into the glass to facilitate the resistivity measurements. It was decided to evaluate the shape factor, area ÷ length, for each section from observations made when the gallium was in the molten state, and this necessitated a knowledge of the electrical resistivity of molten gallium.

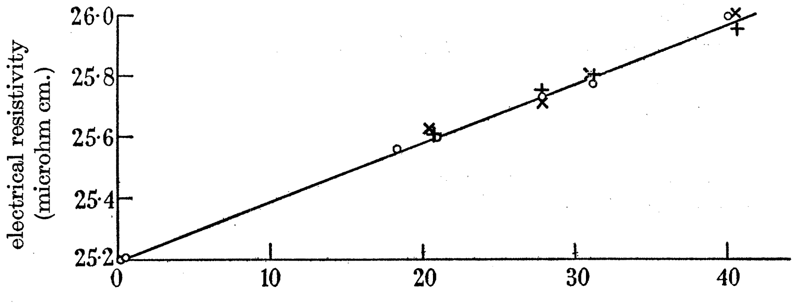

FIGURE 4. Variation of the electrical resistivity of molten gallium with temperature. × Potential length 2 cm. approximately. + Potential length 3·5 cm. approximately. ○ Potential length 14 cm. approximately.

For the purpose of this determination a glass U-tube having four platinum electrodes fused into each limb was filled with clean re-distilled mercury, for which the electrical resistivity values given in Kaye & Laby's *Tables* (9th edition) were assumed. Measurements of the potential drop produced by a known current were made over the temperature range 19 to 28° C and these gave values of A/L for various pairings of the platinum electrodes. The U-tube was then filled with liquid gallium, after being thoroughly cleaned to remove all traces of mercury, and the resistivity measurements were carried out over the range 0° to 40° C. The values obtained, using three different pairs of potential tappings, are plotted in figure 4. These individual values will be seen to agree to within 0·12 % with the straight line

$$\rho_T = 25{\cdot}2(1+0{\cdot}000754T), \qquad (5)$$

where ρ_T is the resistivity at T° C, expressed in microhm cm. units.

Specimen Ga 13

The glass tubing previously referred to, in which the next specimen, Ga 13, was to be grown, was mounted vertically in a room thermostatically controlled at a temperature of about 30° C. From observations of the potential drop produced on each section by a known current and the electrical resistivity of the molten gallium, as given by figure 4, the shape factor of each of the twelve sections was determined. The temperature of the room was then lowered to about 28° C and solidification initiated by the insertion of the sharp point of another seed crystal into the exposed upper surface of the liquid gallium. The seed crystal was again set so that the axial line through the well-defined point was approximately vertical and therefore parallel to the direction of the first section. It was noted that one of the faces of the crystal and one of the sides of its square top was roughly parallel to section 2. Solidification proceeded slowly, requiring several hours for its completion. Electrical resistivity values for each section were then determined at temperatures of 27, 22 and 20° C, and, from the plots of these points, the values given in table 2 for the temperature of 20° C were obtained.

It was convenient to choose a set of orthogonal axes of reference, and, in preparing table 2, sections 13·1, 13·2 have been assumed to coincide with the Y, and X axes respectively. The measured angle between sections 13·2 and 13·5 was 88° 54′ so that section 13·5 coincides approximately with the Z axis.

Figure 5 shows specimen Ga 13 drawn in perspective.

TABLE 2. ELECTRICAL RESISTIVITY DATA AT 20° C FOR VARIOUS SECTIONS OF SPECIMEN GA 13

(ϕ = angle between section 13·1 and other sections in same plane, or angle between section 13·5 and other sections in same plane.)

			electrical resistivity (microhm cm.)	
section no.	plane	ϕ	observed	calculated from equation (6)
13·1	YOX and YOZ	0	55·6	55·4
13·2	YOX	90° 12′	$12{\cdot}0_5$	11·9
13·3		44° 38′	35·4	35·2
13·4		134° 22′	32·3	32·1
13·5	XOZ	0	$13{\cdot}2_5$	13·4
13·6		47° 28′	17·1	17·2
13·7		133° 37′	$7{\cdot}9_5$	$7{\cdot}9_4$
13·8		10° 56′	14·9	15·1
13·9	YOZ	54° 30′	25·5	25·6
13·10		146° 10′	44·2	44·2
13·11		36° 0′	$40{\cdot}0_5$	38·9
13·12	YOZ and YOX	0	55·7	55·4

Just as with the points plotted in figure 3, straight lines could be obtained when the resistivities measured in each of the three mutually perpendicular planes were plotted against $\sin^2\theta$.

From the equations of the three ellipses so obtained the equation of the ellipsoid containing them was derived. The equation of this ellipsoid was

$$0{\cdot}9311x^2+4{\cdot}315y^2+1{\cdot}035z^2-0{\cdot}1767xy+0{\cdot}3191yz+0{\cdot}7195xz = 0{\cdot}07787. \qquad (6)$$

Resistivity values calculated from this equation are included in the last column of table 2.

Referred to its principal axes the equation of this ellipsoid is

$$17{\cdot}27x^2 + 55{\cdot}53y^2 + 7{\cdot}85z^2 = 1 \tag{7}$$

indicating that the resistivity values in the direction of the principal axes are $55{\cdot}5_3$, $17{\cdot}2_7$ and 7·85 microhm cm. i.e. the electrical conductivities of gallium for the three mutually perpendicular axial directions are in the ratios of 1 : 3·2 : 7. The sum

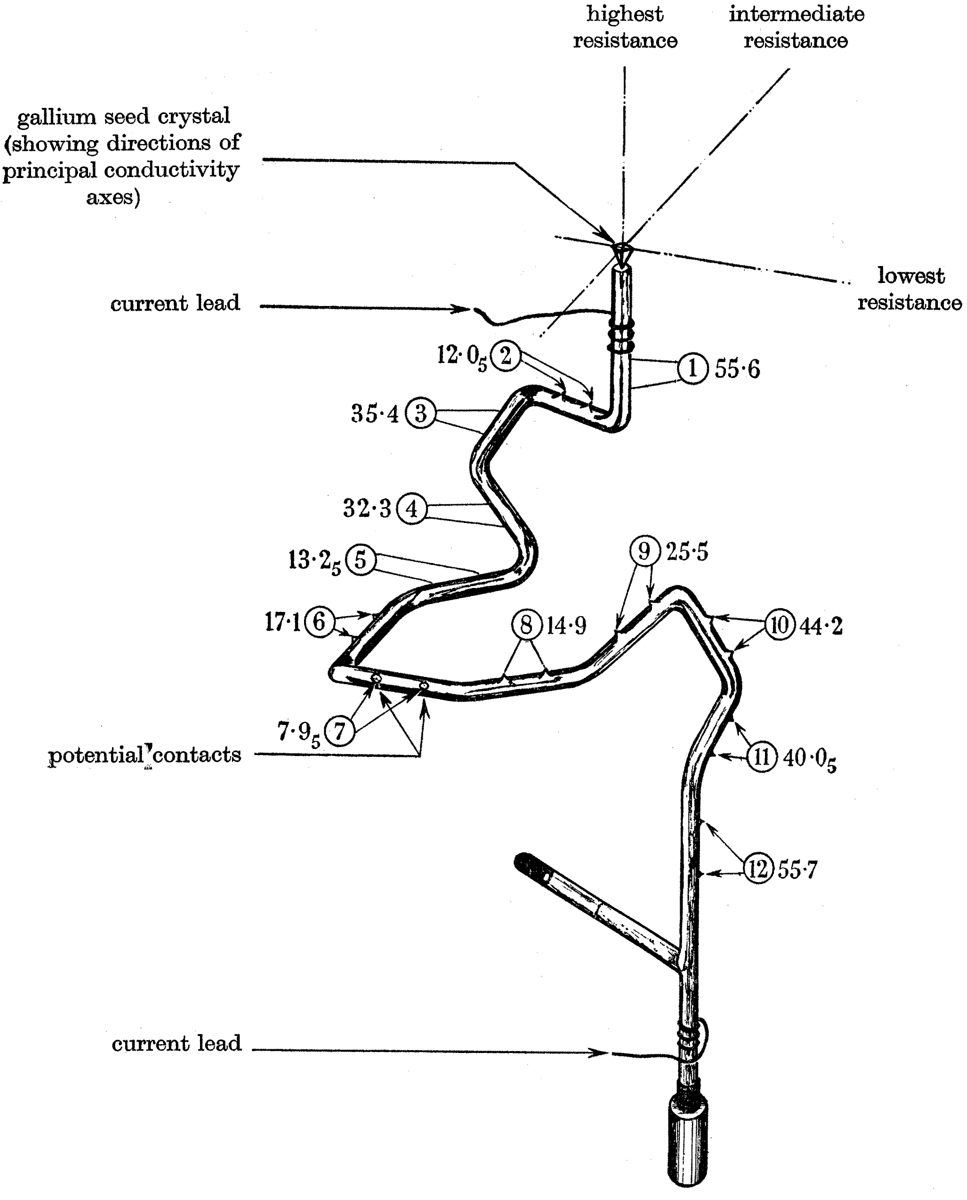

FIGURE 5. Sketch of specimen Ga 13 grown in bent glass tubing and showing electrical resistivity (microhm cm.) of each section at 20° C.

of these values, namely $80{\cdot}6_5$, is of the same order as that previously obtained for three orthogonal directions.

The directions of the principal axes can also be determined and related to the geometry of the seeding crystal. The high resistivity axis is found to coincide with the geometrical axis passing through the well-defined crystal point, whilst the other two axial directions coincide with the diagonals of the approximately squared-topped pyramid.

From table 2 it will be seen that sections 13·1, 13·6 and 13·7 correspond fairly closely with the three axial directions.

The measurements made at the three different temperatures yielded approximate values for the temperature coefficients of resistance of these sections. The values obtained indicate that this coefficient also varies with direction, being of the order of 0·0038 for the high-resistivity direction and of the order of 0·0043 for the other two directions.

From the foregoing results for the resistivity in the three axial directions the specific resistance of polycrystalline gallium is deduced to be $14{\cdot}7_7$ microhm cm. at 20° C and $15{\cdot}4_0$ at $29{\cdot}7_5$° C. Hence, at its normal melting-point, the ratio of the specific resistance of the liquid to that of the solid is 1·67. Since the atoms might be regarded as being randomly distributed in the liquid state, Perlitz (1926) considered that there should be some correlation between the change of resistance on fusion and the crystal form of the solid. Gallium is now shown to come between the alkali metals having body-centred cubic lattices for which the ratio is about 1·5 and the metals with close packed face-centred cubic or hexagonal lattices for which the ratio is approximately 2. From this it would seem that polycrystalline gallium can no longer be classed with bismuth and antimony, for which the ratio is about 0·5 and would thus become an exception to the suggestion made by Bridgman (1921*b*) that the change of resistance on fusion is such that the phase with the smaller specific volume has the smaller specific resistance.

This experiment was accepted as completely confirming that single crystals of gallium exhibit a remarkable degree of anisotropy as regards their electrical conducting properties. Of the good conducting metals so far studied tin comes next to gallium with extreme conductivity ratios of 1·4 to 1, although the poorly conducting metal tellurium has a ratio of 2·75 : 1.

X-RAY DETERMINATION OF CRYSTAL STRUCTURE OF GALLIUM

The most recent determination of the crystal structure of gallium was carried out by Bradley (1935), who concluded that eight atoms of gallium occupy an orthorhombic unit cell of dimensions $a = 4{\cdot}5167$, $b = 4{\cdot}5107$, $c = 7{\cdot}6448$. These dimensions would be in kX units so conversion to Ångstrom units gives $a = 4{\cdot}5258$, $b = 4{\cdot}5198$ and $c = 7{\cdot}6602$. The space-group is V_h^{18} and the atomic co-ordinates are

$$(m0p)\,(m+\tfrac{1}{2},\tfrac{1}{2},\bar{p})\,(\bar{m}+\tfrac{1}{2},\tfrac{1}{2},p)\,(\bar{m}0\bar{p})\,(m,\tfrac{1}{2},p+\tfrac{1}{2})\,(m+\tfrac{1}{2},0,\bar{p}+\tfrac{1}{2})$$
$$(\bar{m}+\tfrac{1}{2},0,p+\tfrac{1}{2})\,(\bar{m},\tfrac{1}{2},\bar{p}+\tfrac{1}{2}),$$

where $m = 0{\cdot}0785 \pm 0{\cdot}0005$ and $p = 0{\cdot}1525 \pm 0{\cdot}0005$.

It follows that each atom has 1 neighbour at 2·442 ± 0·01 Å,
2 neighbours at 2·711 ± 0·003 Å,
2 neighbours at 2·742 ± 0·003 Å,
2 neighbours at 2·801 ± 0·004 Å.

The structure appears to consist of deformed sets of hexagonal rings, whilst Laves (1933) has suggested that the closest pairs of atoms may be regarded as Ga_2 molecules. This last idea would reduce the structure to four such molecules per cell, lying symmetrically in the $a-c$ plane at angles of $\pm 17°$, approximately, to the c axis, the spacing of these molecular planes being $b/2$.

There appear to be no outstanding features in these published data and conclusions which would serve to explain the present anisotropic results and would indicate how the resistivity data are related to the crystallographic axes.

X-ray examinations of some of the gallium single crystals were accordingly undertaken by Mr E. A. Calnan of the Metallurgy Division.

The first crystal to be examined was one of the seed crystals, showing four well-developed pyramidal faces which had already been used to initiate a crystal, and for which resistivity values were known in relation to the crystal setting.

Back reflexion Laue patterns were obtained with the beam directed along the pyramid axis of the specimen. These Laue patterns showed elements of fourfold symmetry, confirming that the pseudo-fourfold axis was within about 1° of the geometrical axis of the crystal. Thus, the observations confirmed that the axis of the seed-crystal, which had invariably been set parallel to the direction of the first section of the solidifying specimen, coincided with the c axis of the gallium crystal.

Complex asterism of the Laue spots, which indicated that the seed crystal was far from perfect, precluded any possibility of distinguishing between the a and b axes for this specimen. It was thought that some straining when the crystal was detached from the specimen grown from it may have caused the deformation to which the asterism corresponded. Accordingly, the X-ray observations were next made on a similar crystal taken freshly from the melt and not used for seeding. With this specimen it was again possible to determine the pseudo-fourfold axis and in addition a method was derived which gave the individual orientations of the a and b axes from the same Laue pattern.

A little asterism of the reflexions still persisted, and this was believed to be due to strains occurring during the process of growth from the super-cooled melt. For the markedly pyramidal crystals are only formed when the liquid metal is super-cooled by 10° C or so. This view was later confirmed by the observation of almost perfectly sharp spots in the pattern obtained for a plate-like crystal grown from a melt where very little super-cooling had been allowed to occur.

Measurements of the electrical resistivity of specimens seeded with the X-ray pyramidal crystal showed the b axis to correspond with the direction of highest conductivity. The same conclusion was reached as the result of the following simple test made on the plate-form crystal. The crystal was cooled with liquid oxygen so as to become frost covered. The head of a warmed pin was then touched on its surface. This caused a small area of frost to melt. The clear frost-free area was an ellipse with the major axis parallel to the direction which the X-ray tests had shown to be that of the *b* axis.

Thus the principal axes of the conductivity ellipsoid, for which the electrical conductivities are in the ratio 1 : 3·2 : 7, have been identified as the *c*, *a* and *b* axes of the gallium crystal.

It is felt that, whilst the lowest conductivity occurs for the direction having the greatest lattice spacing and the highest conductivity for the direction with the smallest spacing, more is needed than the small difference of some 6 parts in 4500 to explain the 2·2-fold conductivity difference between the *a* and *b* directions. The suggestion made by Laves, that the closest pairs of atoms form Ga_2 molecules, might afford an explanation. On this basis, the good conductivity axis would be normal to the molecular plane, whilst the intermediate and low conductivity axes would be in this plane with the molecules alined at angles of approximately ± 73° and ± 17° to the respective conductivity axes.

MEASUREMENTS ON RODS GROWN IN OR NEAR THE AXIAL DIRECTIONS

Three crystal rods, to be referred to as Ga 14·2, Ga 14·4 and Ga 14·5 were then grown in $\frac{1}{6}$ in. bore rubber tubing. Each rod was approximately 6 in. in length.

Ga 14·2 was seeded in the normal manner to have its length parallel to the *c* axis.

Ga 14·4 was grown to have its length approximately parallel to one of the diagonals of the pyramid base. This was done by having a 90° bend in the tubing, initiating the growth as before in the direction of the *c* axis and arranging that beyond the bend the rubber tubing was in the required direction. This portion of the tubing was sheathed in glass tubing to keep it straight.

Ga 14·5 was grown in a similar manner in the third axial direction.

The following determinations, some of a preliminary nature, were made on these specimens.

(*a*) *Electrical resistivity*

The room temperature resistivities of these rods were measured and found to have the values given in table 3. The last column shows the degree of agreement obtained with the anticipated values for the axial directions and it is to be concluded that the rods are single crystals of gallium and that each has been grown in directions which conform to the crystal axes to within 10 degrees.

TABLE 3. ELECTRICAL RESISTIVITIES AT 20° C FOR THREE RODS GROWN TO APPROXIMATE TO THE AXIAL DIRECTIONS

reference no.	approximate axial direction	electrical resistivity at 20° C (microhm cm.)		difference (%)
		observed	calculated	
Ga 14·2	*c*	54·3	$55{\cdot}5_3$	−2·3
Ga 14·5	*a*	17·4	$17{\cdot}2_7$	$0{\cdot}7_5$
Ga 14·4	*b*	8·1	$7{\cdot}8_5$	3·2

The dependence of electrical resistivity on temperature has also been studied for these three rods. In the first instance the measurements were made down to liquid-oxygen temperatures. Subsequently the investigation was extended to considerably lower temperatures, but this aspect of the work forms the subject of a separate paper (Olsen-Bär & Powell 1951).

In making the measurements at liquid-oxygen temperatures the specimens were immersed in a flask of liquid oxygen. To cover the range from −183° C to normal temperatures the specimen, fitted with electrodes and thermocouples which could also serve as potential leads, was placed in a closed ended silica tube, inserted in a larger tube containing paraffin and the whole assembly cooled with the liquid oxygen. Resistivity measurements over a range of temperatures could be satisfactorily obtained during the slow cooling of the specimen, or as it warmed up after removal from the liquid oxygen.

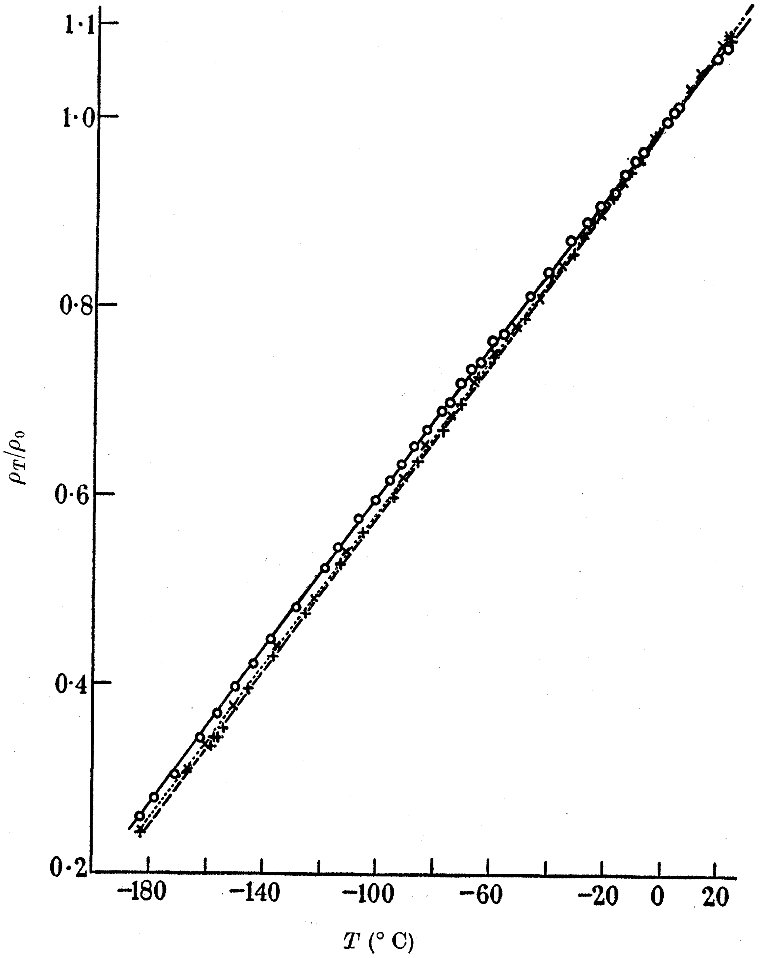

FIGURE 6. ρ_T/ρ_0 down to temperature of liquid oxygen for three gallium rods approximating to the axial directions. Specimen number Ga 14·2 –o–o– for which $\rho_0 = 50{\cdot}3$ microhm cm. Specimen number Ga 14·4 --×--×-- for which $\rho_0 = 7{\cdot}5$ microhm cm. Specimen number Ga 14·5 –+–+– for which $\rho_0 = 16{\cdot}0_5$ microhm cm.

Curves showing the variation of the resistivity down to −70° C are included for the three specimens in figure 1, whilst values for ρ_T/ρ_0, i.e. the ratio of the resistivity at T° C to the resistivity at 0° C, are plotted in figure 6 down to a temperature of

-183° C. The points are seen to lie on three distinct curves each appearing to consist of two straight lines intersecting in the region of -50° C to -60° C. Ga 14·2 shows the least change in resistance with change in temperature and Ga 14·5 the greatest although there is but a small difference between Ga 14·5 and Ga 14·4. Over the temperature range 0 to 20° C the temperature coefficients are in agreement with the preliminary values suggested by the measurements made on specimen Ga 13 and over the range -183 to 0° C the values for the three rods are $0{\cdot}0040_5$ for Ga 14·2, $0{\cdot}0041_2$ for Ga 14·4 and $0{\cdot}0041_6$ for Ga 14·5.

(*b*) *Thermal conductivity*

Precise determinations of the thermal conductivities of these and other gallium specimens have yet to be made. Preliminary comparisons by means of a modified Ingen-Hausz method (1789) have however indicated that the ratios of the thermal conductivities for the three axial directions are of the same order as those for the electrical conductivities. The three specimens were mounted vertically with their lower ends melted into slightly oversized holes in a copper block. The latter was cooled by partial immersion in solid carbon dioxide. The projecting gallium rods were cooled and condensation occurred on portions below the frost and dew points. The thermal conductivities are proportional to the squares of the lengths of rod covered with frost or dew. This test was only used to demonstrate the large differences in thermal conductivity but further comparison against a steel rod of the same diameter and of known thermal conductivity indicated that the thermal conductivities for the three axial directions are of the order of 0·2, 0·4 and 1 joule/sec.cm.°C.

Two further tests have been used which demonstrate the anisotropic thermal conducting properties of gallium. One application has already been referred to in the section on X-ray analysis in connexion with the identification of the *b* axis of the plate-form crystal as the good conducting direction.

The other application is similar but is more appropriate to the large single crystals of gallium which can be readily grown as flat plates if a pool of the super-cooled liquid formed on a glass plate is inoculated with the solid. When the *c* axis of the seeding crystal was vertical and normal to the liquid surface the growth of the solidified area could be watched as a gradually expanding square with its diagonals parallel to the *a* and *b* axes. After complete solidification the crystal was removed from the plate and locally cooled by means of a piece of solid carbon dioxide. This again caused frost to form on that portion of the gallium surface which was cooled below the frost-point. The frost-covered area was a clearly defined ellipse with the major axis parallel to the *b* axis of the crystal and the minor axis parallel to the *a* axis.

When the plate-form crystal was grown in the above way but with either the *a* or *b* axis of the seeding crystal vertical the contours of the solidifying portion were approximately hexagonal. Frost ellipses could be obtained in a similar manner and these confirmed the thermal conductivity to be least in the direction of the *c* axis and greatest in the direction of the *b* axis.

Simple tests of the foregoing type are useful for the identification of the axial directions of a crystal and also for confirming that this direction remains the same at all points on the surface, thus showing the sample to be a true single crystal.

(*c*) *Mechanical properties*

The actual measurements have not yet been made to determine how the mechanical properties vary with crystal direction. Certain marked differences have, however, been noted when handling the specimens.

The thin flat plate crystals were found to bend easily about the *a* axis but were stiffer and tended to snap on attempting to bend about other directions.

On pulling rod-form crystals those grown with their lengths parallel to the *a* axis have tended to give a brittle fracture but definite slip to form a chisel-like fracture occurs with crystals grown in other directions.

(*d*) *Expansion coefficients*

Observations of the change of length with temperature over the range 29 to – 180° C are plotted in figure 7. These determinations were made at the same time as those of electrical resistivity from readings of a dial gauge graduated in one-thousandths of an inch and actuated by a rod of silica resting on the top of the specimen.

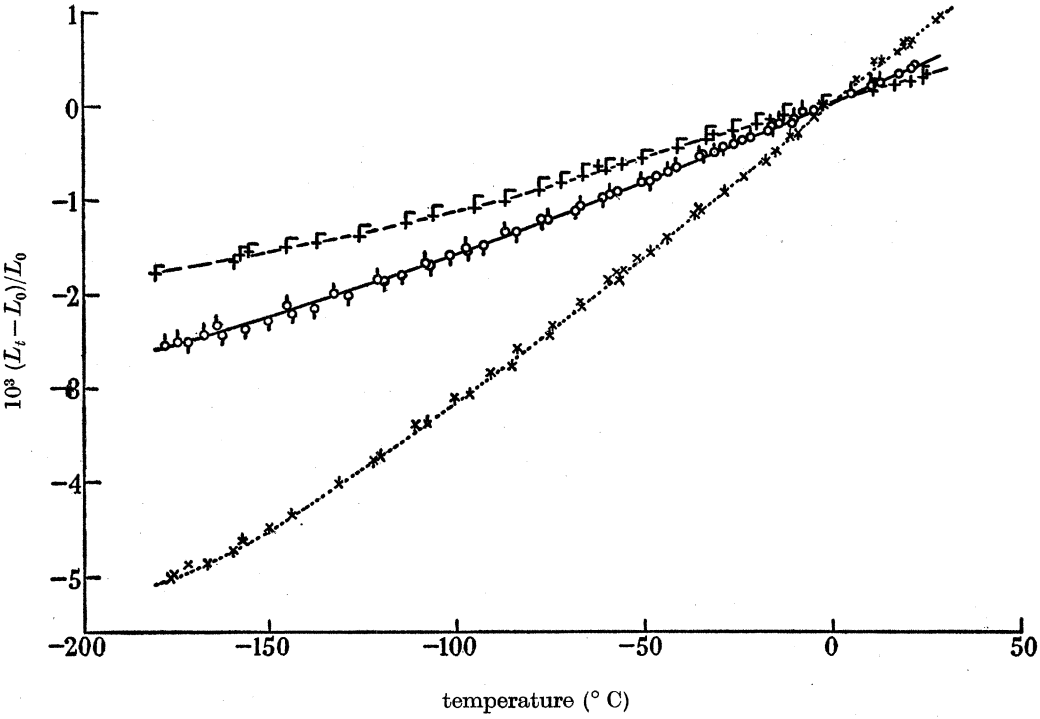

FIGURE 7. Change of length with temperature for three gallium rods approximating to the axial directions. Specimen number Ga 14·2 –○–ȯ–ọ– (3 experiments). Specimen number Ga 14·4 -- × -- ⋇ -- ⋇ -- (3 experiments). Specimen number Ga 14·5 — + — ∓ — (2 experiments).

It will be seen from these results that the thermal expansion is another anisotropic property. Linear thermal expansion coefficients derived from these curves for various temperature ranges are given in table 4.

Table 4. Linear thermal expansion coefficients (cm./cm. °C) of gallium for various temperature ranges

specimen	approximate axial direction	$10^5\times$ linear thermal expansion coefficients (cm./cm.° C) −180 to 0° C	−150 to 0° C	−100 to 0° C	−50 to 0° C	0 to 20° C
Ga 14·2	*c*	$1{\cdot}4_5$	1·5	1·6	$1{\cdot}6_5$	$1{\cdot}6_5$
Ga 14·5	*a*	1·0	$1{\cdot}0_5$	$1{\cdot}1_5$	$1{\cdot}1_5$	$1{\cdot}1_5$
Ga 14·4	*b*	2·8	3·0	$3{\cdot}1_5$	3·2	$3{\cdot}1_5$
approximate value for polycrystalline metal		$1{\cdot}7_5$	$1{\cdot}8_5$	$1{\cdot}9_5$	2·0	2·0

Comparison with other results

The most surprising of the previous electrical resistivity determinations has been that of de Haas & Blom (1937*a*). As already stated, these workers failed to find any measurable difference in the specific resistances for the three axial directions. On the supposition that the lower purity of their gallium might be responsible for the difference, some tests were made with gallium to which 0·11 % of indium had been added. This gave resistivity values of 55·1, 17·5 and 8·1 microhm cm. for the three axial directions at normal temperatures. As a more extreme test, a 'plate' crystal was grown from some gallium residues to which mercury, indium and zinc were known to have been added. This crystal gave the usual frost ellipse. Thus the anisotropy of gallium persists even in the presence of considerable impurity. Realizing that the gallium used by de Haas & Blom would differ in its origin and would certainly not have been extracted from flue dust a similar test was made using gallium from an entirely different source, namely from the mineral ore germanite. This sample of gallium also gave the usual frost ellipse, so it is felt that there is no doubt that the anisotropic properties which have been observed are characteristic of the gallium single crystal.

Another discrepancy has since appeared. This is between the results of the present investigation for the resistivity of liquid gallium and those published subsequently by Dodd (1950). Dodd gives a higher value for the specific resistance at 0° C, $27{\cdot}2_3$ compared with 25·2 microhm cm. and a larger temperature coefficient, 0·001089 compared with 0·000754.

Here again it is difficult to understand the occurrence of an error in the observations of the present investigation. The values obtained for different potential lengths agree closely (see figure 4). Furthermore, an independent check is provided by the various sets of orthogonal crystals of solid gallium. The sum of the resistivities for the sets included in specimen Ga 13 were 80·65 microhm cm. These were based on the resistivity of molten gallium and agreed with other values where actual dimensions were measured which ranged from $80{\cdot}8_5$ to 82·8 microhm cm. Had Dodd's value for the resistivity of molten gallium been used, the sum for Ga 13 would have been 87·2 microhm cm. and this is of a noticeably different order.

The present values for the liquid state are seen from figure 1 to be in close agreement with those of Bridgman (1921 *a*) both as regards absolute value and the temperature coefficient.

Two earlier determinations of the coefficient of cubical expansion of solid gallium have been published and these yield rather lower values than those derived by summation of the linear coefficients given in table 4. Richards & Boyer (1921) obtained a value of 55×10^{-6} between the temperatures of 0·1 and 29·65° C, whilst Klemm (1931) obtained a value of $(53 \pm 5) \times 10^{-6}$ for the range $-78{\cdot}3$ to 18° C.

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