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Electrical resistivity of gallium single crystals at low temperatures

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Electrical resistivity measurements on single crystals of gallium grown to conform approximately to the three axial directions have been extended to low temperatures, detailed investigation being made over the range 20·4 to 4·2° K. The anisotropy of this property increases in this region where the resistivity ratios for the three specimens are approximately 1 : 2·1 : 8 compared with $1 : 2\cdot1_6 : 6\cdot5_5$ at room temperature. The 'ideal' resistivity is proportional to T^n, where $n \simeq 4\cdot45$ for the range 5 to 12° K and decreases to about 3·9 for the range 12 to 20·4° K. The characteristic temperatures as derived from Grüneisen's expression show relatively small differences for the three axial directions but decrease with decrease in temperature. Comparable variations with temperature are observed in the characteristic temperatures derived previously from specific heat measurements on gallium.

Introduction

It was considered of interest to continue the electrical resistivity measurements on single crystals of gallium to the lowest possible temperatures. The present paper describes the first stage of this extension, which was undertaken at the Clarendon Laboratory, Oxford.

Some initial experiments were made in a Linde-type cryostat on the three Ga 14 specimens referred to in Powell (1951). Results for these specimens are given down to temperatures obtainable with liquid hydrogen, but the decrease in resistivity continued to lower temperatures and indicated that specimens of higher resistance would be preferable for this range. Descriptions are given of the preparation of these additional specimens at the National Physical Laboratory and of the resistivity measurements subsequently made at the Clarendon Laboratory.

Preliminary observations on original specimens

The electrical resistivity values furnished by the preliminary observations made on specimens Ga 14·2, Ga 14·4 and Ga 14·5 are set out in table 1.

Table 1. Preliminary resistivity observations to temperature of liquid hydrogen

temperature		Ga 14·2		Ga 14·5		Ga 14·4	
° C	° K	$10^6\rho_T$	$\rho_T/\rho_{0^\circ\mathrm{C}}$	$10^6\rho_T$	$\rho_T/\rho_{0^\circ\mathrm{C}}$	$10^6\rho_T$	$\rho_T/\rho_{0^\circ\mathrm{C}}$
			at N.P.L.				
20	293·15	54·3	1·080	17·4	1·084	8·1	1·083
0	273·15	50·3	1·000	$16\cdot0_5$	1·000	$7\cdot4_8$	1·000
$-182\cdot9_5$	90·2	13·2	0·262	$3\cdot9_5$	0·246	$1\cdot8_8$	0·251
			at C.L.				
$-182\cdot9_5$	90·2	13·1	0·260	$3\cdot9_3$	0·245	$1\cdot8_6$	0·249
−195·8	$77\cdot3_5$	10·3	0·206	$3\cdot0_8$	0·192	$1\cdot4_8$	0·198
$-252\cdot7_5$	20·4	0·4	0·008	$0\cdot1_1$	0·007	$0\cdot05_2$	0·007

The fall in resistivity had caused the sensitivity to become small at 20·4° K, the normal boiling-point of hydrogen. Furthermore, the resistance of each specimen was still decreasing rapidly, as was shown by observations obtained after reducing the pressure over the liquid hydrogen, so it was decided to prepare a fresh set of specimens of higher initial resistance.

PREPARATION AND EXAMINATION OF FURTHER SPECIMENS

Three further specimens were grown inside glass capillary tubes of about $\frac{1}{6}$ mm. diameter and 3 cm. long. These tubes had enlarged ends, fitted with current and potential leads of platinum wire. The shape factor of each tube was derived from observations on the gallium when in the liquid phase, and crystals to conform with three axial directions were obtained by seeding in the usual way. The specific resistances of these three specimens at 20° C were 55·2, 17·6 and $8{\cdot}1_6$ microhm cm., giving a total resistivity for three orthogonal directions of $80{\cdot}9_6$ microhm cm., which is of the same order as obtained previously.

These specimens proved unsuitable for the measurements to low temperatures, as on cooling with liquid oxygen the circuit failed, presumably owing to the fracture of the specimen. Subsequent examination of the tubes disclosed that in some instances the gallium appeared to have spread into the glass, as though short fine cracks had opened up parallel to the direction of the capillary.

The decision was then reached to attempt to test the small-diameter specimens as freely exposed wires. In this way, any question of the specimen being tested under the influence of pressure or of strain imposed on it by the surrounding medium would be obviated.

It was eventually found practicable to grow the crystals in paper tubes. These were formed by wrapping cigarette paper on a length of fine steel wire. The surface was rendered impervious to air by applying a coating of celluloid solution, which was allowed to set before the wire was withdrawn.

The liquid gallium could be drawn into these tubes and seeded in the usual way, the seed crystal being mounted so as to give the required axial crystal direction. Current and potential leads of fine copper wire were usually attached to the specimen whilst it was still wrapped in paper. The tube helped to retain the gallium in position when the slightly warmed wires were introduced. The celluloid was then removed by soaking in amyl acetate, and the paper could be gently brushed off after soaking in water. The gallium specimen was then mounted on a small former of electrical insulating material and was retained in position by securing the leads to the former.

Preliminary observations of the electrical resistivity of each specimen were made at room temperature, 0° C, and at the boiling-point of oxygen. Then the measurements at Oxford were made. These included observations at the boiling-points of oxygen, hydrogen and helium, with a detailed exploration over the lower temperature range. The Oxford measurements were of a comparative character, so the two sets of observations at the oxygen boiling-point made it possible for specific resistance values to be obtained over the whole range.

The three specimens which were used for resistivity observations to low temperatures were numbered Ga 21·1 B, Ga 21·3 B and Ga 26·2.

Table 2 contains details of these three specimens and of their specific resistances at 20, 0 and 183° C.

TABLE 2. DETAILS OF GALLIUM SPECIMENS PREPARED FOR MEASUREMENTS TO 4° K

specimen no.	potential length (cm.)	diameter (cm.)	axial direction (approx.)	specific resistance (microhm cm.) 20° C	0° C	−183° C	ρ_{-183}/ρ_0
Ga 21·3 B	5·90	0·0806	*c*	53·3	49·5	12·9	0·260$_5$
Ga 26·2	6·11	0·0808	*a*	17·5	16·0$_6$	3·9$_6$	0·246$_5$
Ga 21·1 B	6·18	0·0758	*b*	8·1	7·4$_5$	1·8$_7$	0·251

From Powell (1951) it will be seen that at 20° C the calculated resistivities for the three axial directions were 55·$_5$, 17·$_3$ and 7·8$_5$ microhm cm. respectively. The values for the present specimens differ by −4, −1·1 and 3·2 %, and suggest that the axes of the three specimens are within approximately 12, 5 and 7 degrees of the crystallographic axes.

The values for ρ_{-183}/ρ_0 included in the last column will be seen to agree to within 1 % with corresponding values for the previous set of specimens listed in table 1.

RESISTIVITY MEASUREMENTS MADE AT THE CLARENDON LABORATORY

The technique used for these measurements was essentially the same as that described by MacDonald & Mendelssohn (1950). A departure from this previous work was to cover the temperature range from the normal boiling-point of liquid hydrogen (20·4° K) to about 10° K by a slow expansion of the helium gas in the high-pressure chamber of the cryostat. In earlier experiments this temperature region has been covered by adjusting the rate at which the condensed hydrogen was pumped off. However, it was found that a better temperature equilibrium is maintained in the cryostat by using the expansion technique. It was even possible to reach the boiling-point of liquid helium in a single expansion from 20·4° K provided a sufficiently high initial helium pressure ($\sim$ 120 atm.) was used.

To carry out measurements below 4° K a second liquefaction in the conventional manner, expanding from 12° K, was made.

Determination of temperature and resistivity was identical with that of the previous work.

RESULTS

Figure 1 contains the experimental values for each of the three specimens, in which the ratio of the electrical resistivity at T° K to that at the normal boiling-point of liquid oxygen is plotted against temperature. Room-temperature dimensions have been used throughout.

It will be seen that the points for specimen Ga 21·3 B, which approximated to the *c*-axial direction, lie on a curve which is distinctly higher than the curves for the other two specimens. The latter are in close agreement with each other, so that the results now obtained for the liquid-hydrogen to liquid-helium range resemble those previously obtained from room temperature to liquid oxygen.

Residual resistances were derived for each specimen from the shapes of the curves in the liquid helium region, and the 'ideal' specific resistance, $[\rho_T]$, was obtained by subtracting the residual resistance according to Matthiessen's rule. The values of the residual resistivities, expressed as a ratio to the resistivity at the ice point, are included in table 3. This table gives similar data for the specimens used by de Haas & Voogd (1929, 1931) and by de Haas & Blom (1937). From these results it would seem that the net effects of impurities and other imperfections is least for the present samples and is of the same order for all three samples. The other

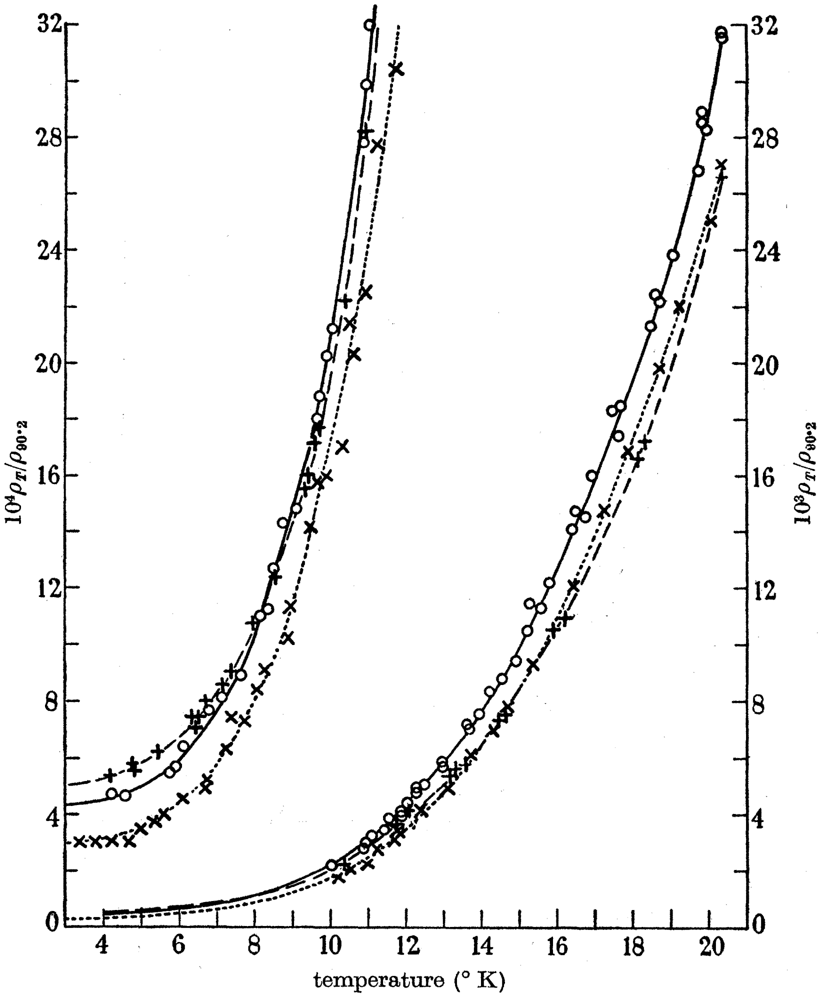

FIGURE 1. Variation of $\rho_T/\rho_{90\cdot2}$ with temperature for three gallium specimens approximating to the axial directions. Ga21·3B —○—○— ($\rho_{90\cdot2} = 12\cdot9$ microhm cm.); Ga26·2 – + – – + – ($\rho_{90\cdot2} = 3\cdot96$ microhm cm.); Ga 21·1B ··· × ··· × ··· ($\rho_{90\cdot2} = 1\cdot87$ microhm cm.).

TABLE 3. $[\rho_T/\rho_{273\cdot1_5}]$ FOR VARIOUS GALLIUM SPECIMENS

	de Haas & Voogd	de Haas & Blom (1937)			present work		
T (° K)	(1929, 1931)	$P1$ crystal	$P2$ crystal	$P3$ crystal	Ga 21·3B	Ga 26·2	Ga 21·1B
90·2	2·606 × 10^{-1}	2·592 × 10^{-1}	2·447 × 10^{-1}	2·500 × 10^{-1}	2·605 × 10^{-1}	2·465 × 10^{-1}	2·51 × 10^{-1}
20·4	8·72 × 10^{-3}	7·74 × 10^{-3}	6·93 × 10^{-3}	6·78 × 10^{-3}	8·13 × 10^{-3}	6·42 × 10^{-3}	6·72 × 10^{-3}
14·0	2·30 × 10^{-3}	—	—	—	1·88 × 10^{-3}	1·46 × 10^{-3}	1·55 × 10^{-3}
10·6	—	—	—	—	4·38 × 10^{-4}	3·56 × 10^{-4}	3·61 × 10^{-4}
4·2	(7 × 10^{-6})	—	—	—	9·4 × 10^{-6}	7·7 × 10^{-6}	7·8 × 10^{-6}
residual ratio	3·03 × 10^{-4}	9·9 × 10^{-4}	7·0 × 10^{-4}	5·0 × 10^{-4}	1·11 × 10^{-4}	1·25 × 10^{-4}	0·72 × 10^{-4}

TABLE 4. ELECTRICAL RESISTIVITY AND RESISTIVITY RATIOS FOR GALLIUM SPECIMENS

(The bracketed values express the resistivity of each specimen as a ratio to that of specimen Ga 21·1B)

	specimen no. Ga 21·3B		specimen no. Ga 26·2		specimen no. Ga 21·1B	
temperature (° K)	observed resistivity ρ	'ideal' resistivity $[\rho]$	observed resistivity ρ	'ideal' resistivity $[\rho]$	observed resistivity ρ	'ideal' resistivity $[\rho]$
$293{\cdot}1_5$	53·3 × 10^{-6} (6·58)	—	17·5 × 10^{-6} (2·16)	—	8·1 × 10^{-6} (1·0)	—
90·2	12·9 × 10^{-6} (6·9)	—	3·96 × 10^{-6} (2·12)	—	1·87 × 10^{-6} (1·0)	—
20·4	4·075 × 10^{-7} (8·06)	4·02 × 10^{-7} (8·04)	1·05 × 10^{-7} (2·08)	1·03 × 10^{-7} (2·06)	5·056 × 10^{-8} (1·0)	5·003 × 10^{-8} (1·0)
14·0	9·868 × 10^{-8} (8·19)	9·32 × 10^{-8} (8·09)	2·548 × 10^{-8} (2·11)	2·348 × 10^{-8} (2·04)	1·205 × 10^{-8} (1·0)	1·152 × 10^{-8} (1·0)
10·0	2·718 × 10^{-8} (8·43)	2·17 × 10^{-8} (8·07)	7·72 × 10^{-9} (2·39)	5·72 × 10^{-9} (2·13)	3·223 × 10^{-9} (1·0)	2·69 × 10^{-9} (1·0)
4·2	5·94 × 10^{-9} (10·05)	$0{\cdot}46_5$ × 10^{-9} (8·02)	2·123 × 10^{-9} (3·59)	0·123 × 10^{-9} (2·12)	0·591 × 10^{-9} (1·0)	0·058 × 10^{-9} (1·0)

entries in table 3 enable the values of $[\rho_T/\rho_{273\cdot 1_5}]$ to be compared over the temperature range studied. The agreement is reasonably close, and it is of interest that the three samples tested by de Haas & Blom, which were also stated to conform to the three axial directions, show very similar variations to those of the present investigation.

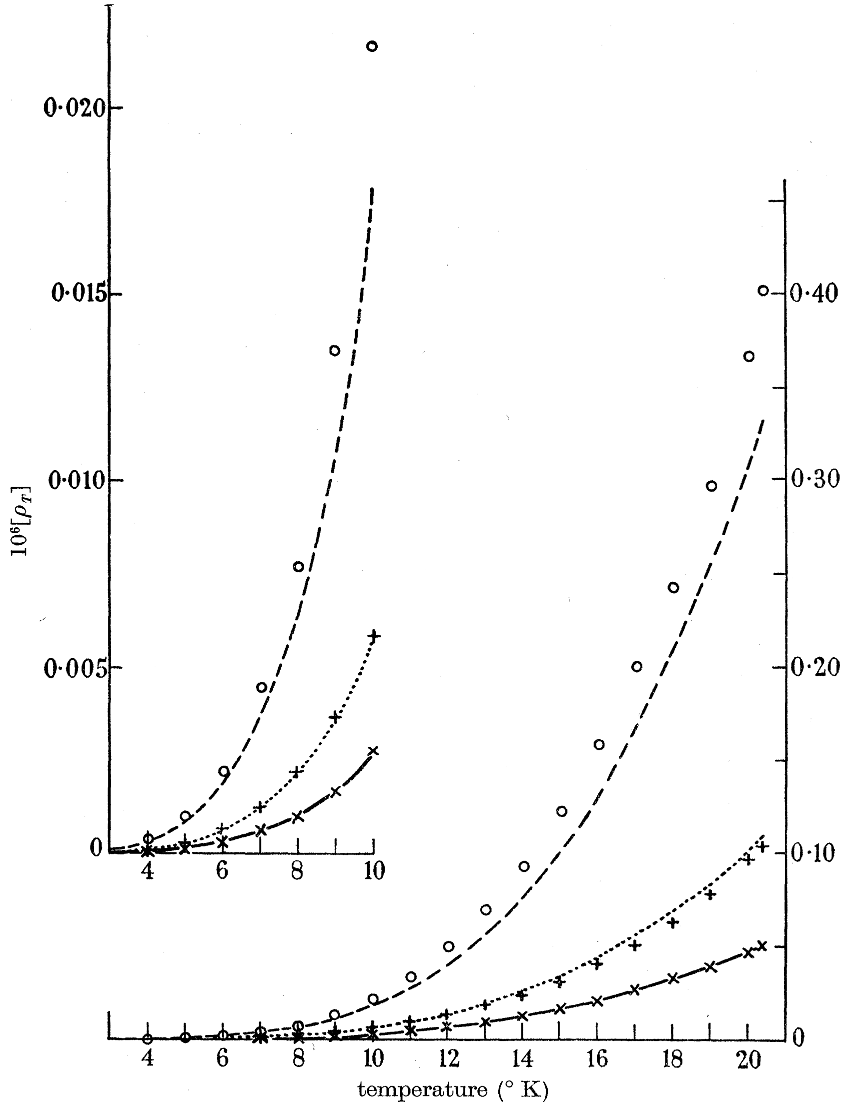

FIGURE 2. Comparison of 'ideal' resistivity changes with temperature for three gallium specimens approximating to the axial directions. ○ Ga 21·3 B (smoothed values); + Ga 26·2 (smoothed values); × Ga 21·1 B (smoothed values).

...... 2·16 × $[\rho_T]$ for Ga 21·1 B,

i.e. $\dfrac{\rho_{293} \text{ for Ga 26·2} \times [\rho_T] \text{ for Ga 21·1 B}}{\rho_{293} \text{ for Ga 21·1 B}}$,

– – – 6·58 × $[\rho_T]$ for Ga 21·1 B,

i.e. $\dfrac{\rho_{293} \text{ for Ga 21·3 B} \times [\rho_T] \text{ for Ga 21·1 B}}{\rho_{293} \text{ for Ga 21·1 B}}$

In figure 2 values of the 'ideal' specific resistance as derived for each of the three specimens from the smooth curves of figure 1 are plotted against temperature. The dotted lines in figure 2 show the resistivity of Ga 21·1B multiplied by 2·16 and 6·58 respectively, the factors which would give agreement with the resistivities of Ga 26·2 and Ga 21·3B at room temperature. It will be seen that for Ga 26·2 the points conform closely with the line up to about 12° K, but at higher temperatures the points are as much as 10 % low; for Ga 21·3B the difference is more pronounced, the points being some 20 to 30 % above the line over the whole range studied. This indicates that the degree of anisotropy of gallium is 20 to 30 % greater over the range 4·2 to 20·4° K than at normal temperatures. Detailed values are given in table 4.

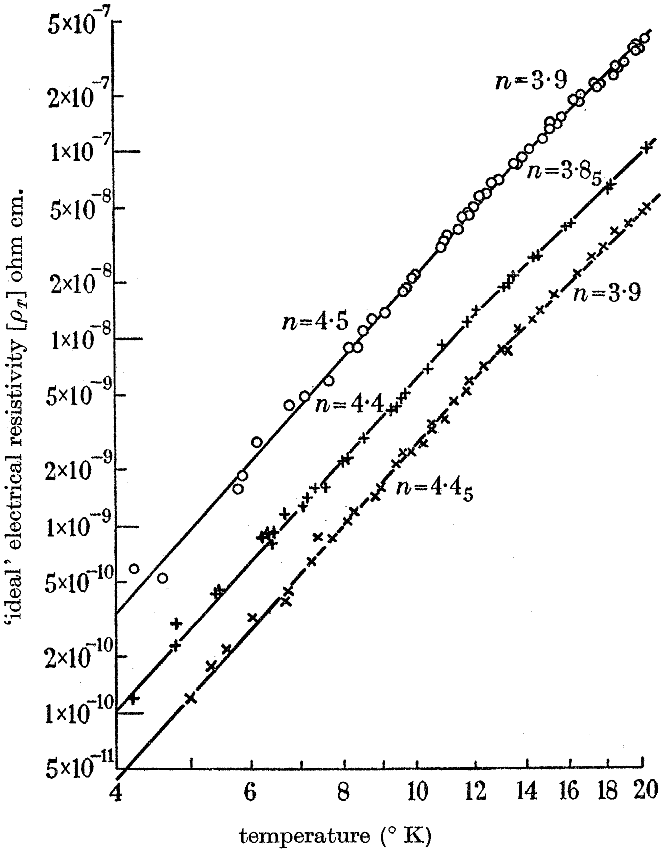

FIGURE 3. Logarithmic plot of variation of 'ideal' resistivity of gallium with temperature. ⊙ Ga21·3B, + Ga26·2, × Ga21·1B.

Logarithmic plots of the 'ideal' resistivity of each specimen against temperature are shown in figure 3. If $[\rho_T] \sim T^n$, then it is seen from the slopes of these lines that for all three specimens $n \simeq 4{\cdot}4_5$ in the temperature range 5 to 12° K. In the region of 12° K the value of n changes to about 3·9.

Thus, at low temperatures, the electrical resistance of gallium varies nearly as in a free electron metal, for which $n = 5$ is to be expected.

Values for the Debye characteristic temperature, θ_D, were evaluated by fitting the ratio $[\rho_T/\rho_{90 \cdot 2}]$ to the expression derived by Grüneisen. Whilst the values so obtained at any one temperature were of similar order for the three specimens there was a considerable variation with temperature. At 20·4° K, θ_D had values of 155, 165 and 163° K for the *c*, *a* and *b* directions respectively, whereas at 6° K the corresponding values were 131, 132 and 135° K.

Blom (1950) considered that the results for the three specimens studied by de Haas and himself required the much higher θ_D values of 210, 230 and 220° K. By using the ratio $[\rho_{90 \cdot 2}/\rho_{273 \cdot 1_5}]$ it is found that the present results give values of the same order, namely, 203, 228 and 219° K, and it seems clear from table 3 that the data of de Haas & Blom would also give lower values at lower temperatures.

When trying to correlate the resistivities with the lattice vibrations, one finds that they can be expressed for all three crystal directions by approximately the same θ_D. The fact that our characteristic temperatures so derived fall by about 25° between 20 and 6° K is in general agreement with the observation of Clusius & Harteck (1928) on the specific heat of gallium. These authors derive a θ_D value of about 225° for the temperature range between 50 and 150° K. They point out that their specific heat values below this range are higher than would correspond to this θ_D, and in fact the θ_D obtained from their lowest value (at 15° K) would be of the order of 165°. Blackman (1951)* has recently pointed out that no agreement must be expected between the characteristic temperature derived from (*a*) the specific heat and (*b*) the change of resistivity with temperature, since the latter is determined by the longitudinal vibrations only. However, as the present work shows, there is in the case of gallium, as indeed in many other metals, close agreement between these two characteristic temperatures. The reason for this correlation which can hardly be accidental is as yet unexplained.

No detailed measurements of the resistance-temperature dependence have been carried out on anisotropic crystals since the work of Grüneisen & Goens, (1924) on zinc and cadmium and the measurements of these authors were confined to a few isolated temperatures above the helium range. The present experiments show that the anisotropy of the gallium crystal is barely noticeable in the variation of resistance with temperature and approximately the same θ_D values have been obtained from measurements along the three crystal axes. However, comparing directly the 'ideal' resistivities at the lowest temperatures, one finds, as mentioned above, that the ratio between the crystal axes increases somewhat. This indicates an increase in the electrical anisotropy on approaching absolute zero. In gallium, as in zinc and cadmium, the lowest conductivity values occur in the direction of the greatest lattice spacing, and the smallest lattice spacing yields the highest conductivity values. Thus the conductivity of these metals decreases with increasing distance between the atoms, which would suggest tighter binding of the electron in the axes with greater lattice spacing.

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The photodecomposition of barium azide

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Results obtained on the rate of photolysis of barium azide and its variation with temperature and light intensity are reported. These are not in accord with Mott's mechanism and an alternative approach involving the production and trapping of excitons is proposed.

We have made a detailed analysis (unpublished) of Mott's (1939) theory of the mechanism of decomposition of metallic azides and concluded that modifications were required. In the present paper we report results obtained on the photolysis of the barium salt and put forward a theory, involving the production and trapping of excitons, which is in accord with both the present results and others to be reported in a further paper and also with those of previous workers (Garner & Maggs 1939; Wischin 1939).

Experimental

Materials

A 3 % aqueous solution of HN_3, obtained by distillation of NaN_3 with H_2SO_4, was neutralized (phenolphthalein) by a suspension of A.R. $Ba(OH)_2$. Addition of