of the peaks in pure iron changed, as expected, to a 9/4:3:3/4 ratio. (The reason for this odd method of writing 3:4:1 is to preserve the normalization to the case of random orientation.) However the spectrum from the 28% Al alloy was the same as with no applied magnetic field. Therefore in calculating the solid curve for this alloy, 9/4:3:3/4 intensity ratios were assumed.

DISCUSSION

The agreement between the calculated curves and the experimental data is sufficiently good that we regard this model, in which the moment per iron atom depends only on the number of aluminum nearest neighbors, as adequate for the present level of experimental accuracy. Our results, however, do not provide a sensitive test of the exact functional relationship assumed [Eq. (1)], particularly in the range of large n. Our experiments were limited to the iron rich end of the diagram and the contribution to the spectra of iron atoms with many aluminum neighbors was quite small. It also seems likely that second and more distant neighbor interactions must have some influence on the internal field, but since the natural width of the peaks is greater than the peak shifts due to the change of one nearest neighbor, the additional blurring due to second neighbor effects would be very difficult to see. Further measurements, including the effects of varying local order, as well as composition, may provide more detailed information about the relation between the local environment of an iron atom and the magnetic field at its nucleus.

The absence of observable broadening in the iron-cobalt and iron-nickel systems[4] is not inconsistent with the model used here. The variation of internal field with composition in these systems is sufficiently small that the broadening due to varying microenvironments would be negligible.

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[4] C. E. Johnson *et al.*, Phys. Rev. Letters **6**, 450 (1961).

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Determination of Contributions to the Residual Resistivity of Gallium at 4.2°K*

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Resistivity measurements have been carried out on single-crystal wires of high-purity gallium in the temperature range of 1.27° to 43°K, and also at 4.2°K on gallium with added impurities, and with varying wire diameter. The last measurements indicated the electron mean free path to be 1.2 mm at 4.2°K at a resistivity of about 3×10^{-22} esu, implying that the effective number of free electrons per atom in gallium is 0.2. Diffuse surface scattering was found to be an important scattering mechanism in wires of high-purity gallium at 4.2°K, and its contribution to the ratio of resistivity at 4.2 to 295°K in a 1-mm diam crystal is 1.5×10^{-5}. The temperature measurements indicated that no resistivity minimum occurs, and also that along the b axis, the lattice scattering contributes 0.4×10^{-5} to the resistivity ratio. The effect of grain boundaries on the resistivity ratio is negligible. The presence of as little as one atomic part per million of impurities such as Cu, Ag, Zn, Tl, Ge, Sn, Pb, and As can be detected by residual resistivity measurements.

I. INTRODUCTION

THERE are four main contributions to the resistivity of a metal, namely scattering of electrons from the lattice ρ_L, structural defects ρ_D, impurities ρ_I, and the surface ρ_S. To a first approximation, these contributions are independent of each other, and are connected by a simple additive relationship. The effect of lattice scattering, while dominant at room temperature, decreases with decreasing temperature. However, according to Matthiessen's rule, the effect of impurity scattering in metals is approximately temperature independent. The present research is concerned with determining the effect of each of the above contributions in gallium by means of low temperature resistivity measurements.[1]

Measurements have previously been reported on the variation of resistivity of gallium with crystallographic orientation and with temperature.[2,3] The latter measurements have been repeated with gallium having over an order of magnitude fewer impurities, and the previously reported $T^{4.4}$ behavior of resistivity[3] at low temperatures has been confirmed. However, in the present work, a more accurate value of the effect of lattice scattering has been derived, and in addition, the contribution due to specific impurities, structural defects, and diffuse

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[1] L. R. Weisberg and R. M. Josephs, Bull. Am. Phys. Soc. **5**, 430 (1960).

[2] R. W. Powell, Proc. Roy. Soc. (London) **A209**, 525 (1951).

[3] M. Olsen-Bar and R. W. Powell, Proc. Roy. Soc. (London) **A209**, 542 (1951).

surface scattering has been measured.[4] The last measurements provide an estimate of the mean free path of electrons at 4.2°K, and the number of conduction electrons per atom in gallium.

It is noteworthy that since the effect of impurities can be easily separated from the other factors according to their additive relationship, measurements of the residual resistivity of gallium at 4.2°K provide a powerful analytical tool to estimate the impurity content of high-purity gallium. Use of this procedure has already been reported for the evaluation of the purification of gallium by vacuum annealing,[5] and by directional freezing.[6] Knowledge of the purity of gallium is essential in the preparation of semiconducting compounds such as GaAs and GaP.

One of the outstanding characteristics of gallium is its orthorhombic structure leading to a marked anisotropy of many of its properties.[2] However, even though the resistivity is a factor of seven greater along the c axis as compared to along the b axis at 4.2°K, the *ratio* of the resistivity at 4.2°K to room temperature varies by only 20% along the same two axes. The use of the resistivity ratio has other advantages in that it minimizes the effect of crystal uniformity and geometry, so that measurements of crystal diameter and potential lead spacings do not have to be made. Further, the effect of thermal expansion on this ratio is entirely negligible. Therefore, most of the results are expressed in terms of R^*, which is defined as 10^5 times the ratio of resistivity at 4.2°K to that at room temperature. Variations in the resistivity at room temperature due to temperature variations are percentage-wise too small to necessitate establishing the temperature of measurement closer than the usual 22° to 28°C range. When all measurements are expressed in terms of the resistivity ratio, for pure gallium, the relation connecting the four resistivity contributions can be written as

$$R^*=R_L^*+R_D^*+R_I^*+R_S^*. \qquad (1)$$

II. EXPERIMENTAL METHOD

A. Sample Preparation

The gallium used in these studies[7] had a spectrographically determined purity of $>99.999\%$. Gallium single crystals are prepared without contamination in the form of wires by drawing the liquid gallium into small diameter Teflon "spaghetti" tubing with a 0.1-cm^3 capacity syringe. The gallium is next forced out of the Teflon tube until a small amount protrudes from the open end. This droplet is placed in contact with a gallium seed crystal to start the growth, which propagates at a rate of 1 to 2 mm min^{-1}. The growth progression can be easily followed, since the Teflon tubing is translucent, and the solid phase is darker than the liquid. Seed crystals can be prepared quite simply by selecting them from those floating on a slowly solidifying gallium melt. The axial orientation of the gallium wires was, in most cases, close to the a-axis. The gallium crystal can be removed from the tubing without distortion by splitting the tubing longitudinally at one end and pulling simultaneously on both halves, thereby peeling the tubing away from the crystal like the skin from a banana. Gallium wires have been prepared with diameters between 0.4 and 1.8 mm; however, a diameter of 1.0 to 1.1 mm was used for most experiments. Crystals as long as 10 cm were grown, but the average sample length was about 2 cm.

In one series of experiments, samples of gallium were prepared doped with impurities at a level of about 100 atomic parts per million (ppm). The impurity was weighed on a microbalance, and then inserted into a 5 mm bore quartz tube sealed at one end. About 5 g of gallium were then introduced into the tube, and the tube was sealed off under vacuum. The tube was heated to above the melting point of the impurity and held there for one to five hours, with intermittent vigorous shaking. For impurities with melting points in excess of 1000°C, annealing times were reduced to 10 to 30 min to avoid attack of the quartz by the gallium. In the process of heating the gallium, its oxide film was observed to vaporize at about 600°C and condense at the upper part of the tube, where it remained throughout the subsequent heating. To serve as a control, undoped samples of gallium were given similar heat treatments to investigate the possibility of reaction between the gallium and the quartz, but none was observed either spectrographically or by resistivity measurements. In all cases, the quartz tube was quenched in water subsequent to the heat treatment.

B. Sample Holder and Mounting

The sample holder consists of a Teflon mounting piece attached to the end of a 6 mm diam, 80 cm long, thin wall stainless steel tube. Two 0.018-in. and two 0.012-in. diam copper wires pass through the tube to the Teflon piece for current and potential leads, respectively. Two holders have been constructed, the first to hold only one sample, and the second to hold three samples. Each holder is intended for direct insertion into standard liquid helium Dewars, with, respectively, $\frac{1}{2}$-in. and $\frac{3}{4}$-in. i.d. entrance tubes. Contact to the gallium was made by 0.015 in. silver wires. Previous tests showed that of Cu, Pt, W, In, Au, and Ag, the strongest mechanical bond to gallium was formed by the silver, provided the tarnish was removed. To mount a sample, the Teflon holder is placed on a bed of dry ice,

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[4] Preliminary research has also been reported by T. Frederking and R. Reinmann, Helv. Phys. Acta 33, 998 (1960).

[5] L. R. Weisberg, F. D. Rosi, and P. G. Herkart, *Properties of Elemental and Compound Semiconductors*, Metallurgical Society Conferences (Interscience Publishers, Inc., New York, 1960), Vol. 5, p. 45.

[6] R. A. Kramer and L. M. Foster, Annual Fall Meeting, American Chemical Society, New York, September 11–16, 1960 (unpublished), Abstract 79.

[7] Purchased from the Aluminum Company of America.

and the silver wires are bent so they are sprung lightly against the sample. A small soldering pencil fluxed with gallium is held to the silver wire until the conducted heat barely melts the gallium and the silver wire sinks in. The gallium freezes immediately upon withdrawal of the soldering pencil.

In one experiment, a gallium sample was placed in a cryostat for measurements down to 1.27°K. For this case, the gallium was attached to a piece of copper with GE cement No. 7031, which provided both electrical insulation and thermal contact.

C. Experimental Procedure

The usual four-contact method of measuring resistivity was employed. The current was supplied from batteries in series with controlling resistors and a reversing switch. The potential was measured with a commercial Liston-Becker dc amplifier. Stray potentials were eliminated directly in this amplifier by means of a zero setting control; moreover, the potential was measured with the current flowing in the forward and reverse directions. The resistivity was also measured at two values of the current to check on linearity. Using a 1-mm diam sample, typical values for the current and the voltage at room temperature are 10 ma and 20 μv, and at 4.2°K are 2 amp and 0.1 μv. A practical upper limit for the current at 4.2°K was found to be about 5 amp, since at higher currents, anomalously high values of resistance were observed, attributed to heating effects occurring at the contacts.

Measurements were carried out first at room temperature, and then at 4.2°K by inserting the Teflon holder directly into a standard helium Dewar. The holder was first precooled by immersion into liquid nitrogen, which reduced the helium consumption to only 0.2 liter for each dip of the three-sample holder. For the one experiment in which the temperature was varied from 1.27° to 43°K, the sample was placed in a helium cryostat, with provisions for pumping on the helium, and for heating the sample chamber. Temperatures were determined by means of a carbon resistance thermometer placed in good thermal contact with the specimen, and calibrated during the course of the experiment.

D. Experimental Error

For samples with values of R^* above 3, the error in the current and potential measurements was 3%. For samples with lower resistivities, the background potential fluctuations contributed 0.02 μv noise, thereby increasing the error of the potential measurements to as much as 10%. In these cases, the value of R^* could be determined to only within ± 0.2. Greater precision was not attempted since all but one of the experiments required the preparation of a series of equivalent gallium samples. Despite precautions of stirring and cleanliness, the measurements from sample to sample separately drawn from the same batch of gallium were observed to vary by as much as 20%, even in the doped samples. This suggests that these variations are due to differing impurity contents of each sample. Similar effects to even a greater extent were previously observed by spectrographic analysis of a series of gallium samples. The possible 20% error due to variations in orientation was minimized by seeding of the crystal growth. Improper seeding leading to orientations far off the *a* axis were detected in the room temperature value of resistivity and rejected. The high residual total error necessitated the measurement of multiple samples in all experiments, except the measurement of the temperature dependence of resistivity.

III. RESULTS AND DISCUSSION

A. Effect of Crystal Defects

In order to determine the effect of grain boundaries, three gallium samples were prepared from different lots of gallium with a grain boundary between the potential leads. This was accomplished by simultaneously seeding the two ends of the molten gallium in the Teflon tube with seeds of different orientation. In addition, several polycrystalline samples were prepared by rapidly cooling the gallium without seeding. Within experimental error, there was no discernible effect of the grain boundaries on the value of R^*.

It is also necessary to determine the effects of strains induced by handling on the resistivity. Four crystals were grown and mounted, and after measurement were bent back and forth at room temperature about the center as much as 45° from the original axis. There was no observable effect on the resistivity at room temperature, but the resistivity at 4.2°K increased slightly. The results for a typical crystal are that the initial value for R^* of 2.2 increased to 3.4 after one bend, to 3.6 after three bends, and to 4.3 after ten bends. In a separate test, measurements on pieces taken from the front and tail ends of a crystal wire always agreed to within 10%. It can be concluded that the effect of any slight strains introduced during normal careful handling are negligible. It should be remembered that at room temperature gallium is continually being annealed since it is within a few degrees of its melting point (29.8°C) so that the effects of cold work are minimized.

B. Temperature Variation of Resistivity

In order to re-examine the effect of lattice scattering at 4.2°K, the temperature variation of resistivity of a gallium sample was measured from 1.27 to 43°K. The sample had a 1 mm diameter, the potential lead spacing was 4 cm, and the room temperature resistivity was 9×10^{-6} ohm-cm, indicating that its orientation was close to the *b* axis. In Fig. 1 is shown the variation with temperature of the ratio of resistivity at each temperature to the room temperature resistivity. It can be seen that over a limited temperature range the resistivity varied as $T^{4.5}$, which is in good agreement with the value of $T^{4.4}$ previously reported.[3] As indicated in Fig. 1, by subtracting away the residual resistivity the lattice resistivity at 4.2°K is extrapolated to a value of R_L^* of 0.4. A value of R_L^* of 0.8 was found by Olsen-Bar and Powell[3] for a sample oriented along the b-axis, but their extrapolation was less reliable because their gallium was more than an order of magnitude less pure.

It is noteworthy that no rise in resistivity at low temperature was observed for gallium, nor was it observed in less pure gallium.[3] This suggests that gallium, like aluminum,[8] may belong to the class of metals for which no resistivity minimum occurs.

C. Effect of Surface Scattering

The contribution of diffuse surface scattering to the resistivity of thin wires with circular cross sections has been calculated by Dingle[9] and Sondheimer.[10] It can be shown that a good approximation to the results of Sondheimer of the variation of the ratio of total resistivity, ρ, to the resistivity of the bulk ρ_B in the absence of surface scattering, with the ratio of wire diameter, a, to the electron mean free path, l, is given by $\rho/\rho_B=1+l/a$.[11] This relation has several implications, best seen by rewriting the equation as:

$$\rho=\rho_B+\rho_B l/a=\rho_B+\rho_S. \qquad (2)$$

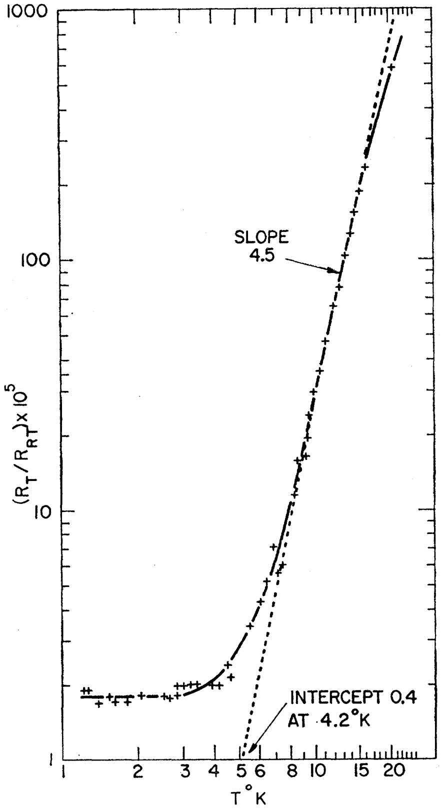

FIG. 1. Temperature variation of the resistivity of gallium divided by its room temperature resistivity.

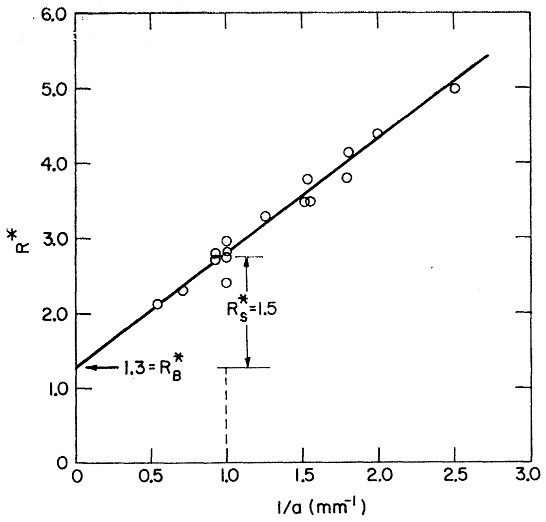

FIG. 2. Variation of R^*, defined as 10^5 times the ratio of resistivity at 4.2°K to that at room temperature, with gallium wire diameter, a.

That is, the total resistivity can be considered as being composed of two additive parts, one due to the bulk, and the other due to surface scattering, ρ_S. Furthermore, the quantity $\rho_S=\rho_B l/a$ is independent of ρ_B since the quantity $\rho_B l$ is roughly a constant for a metal.

Next, it can be seen from Eq. (2) that a plot of ρ vs l/a will have a zero intercept of ρ_B and a slope of $\rho_B l$. Therefore, both the quantities ρ_S and l can be separately determined by varying the diameter of the samples. The results of such an experiment are shown in Fig. 2. It is found that at 4.2°K, $R_B^*=1.3$, $R_S^*=1.5$ at a 1 mm diam, and that $l=1.2$ mm. Using a value of $\rho_B=17\times10^{-6}$ ohm-cm at room temperature,[2] the value of $\rho_B l$ at 4.2°K is found to be 3×10^{-23} esu. Absolute significance cannot be ascribed to the value of either ρ_B or l. First, both of these quantities consist of contributions from lattice scattering and impurity scattering, and their relative contributions vary with temperature. Also, the lattice contributions will be orientation dependent. However, using the simple formula $\rho_B l=(3/8\pi)^{\frac{1}{3}}(h/e^2N^{\frac{2}{3}})$ to provide a crude approximation to the effective number N of free electrons per cm^3, it is found that there are 0.2 electron per atom in gallium.

Because of the marked anisotropy of gallium, it is possible that there is also some contribution due to specular scattering from the surface. While the data are

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[8] M. P. Garfunkel, F. D. Dunnington, and B. Serin, Phys. Rev. **79**, 211 (1950).

[9] R. B. Dingle, Proc. Roy. Soc. (London) **A201**, 545 (1950).

[10] E. H. Sondheimer, *Advances in Physics*, edited by N. F. Mott (Taylor and Frances, Ltd., London, 1952), Vol. 1, p. 1.

[11] Implicit in L. Nordheim, Act. Sci. Ind. No. 131 (Hermann et cie, Paris, 1934), p. 11.

TABLE I. Increase in R^* due to 1 atomic ppm of impurity.

Group	Impurity	ΔR^*
I	Cu	1.8
	Ag	0.18
II	Zn	0.9
III	In	$\leqslant 0.07$
	Tl	40
IV	Ge	1.1
	Sn	0.15
	Pb	1.3
V	As	1.0

insufficient to decide this question it is noted that the curve of R^* vs a, derived from Fig. 2, shows no tendency for saturation at small values of a, which is characteristic of specular scattering.[12]

D. Effect of Impurities

Over fifty samples were prepared with roughly 100 atomic ppm each of fourteen different impurities, following the procedure described in Sec. II A. Subsequent to the measurement of R^*, the samples were analyzed by an emission spectrograph to determine if the impurity entered the crystal. Those impurities which were definitely present in the gallium are listed in Table I, together with the increase in R^* due to one atomic ppm of the impurity. At least two samples were measured from each batch of doped gallium. For the cases of Al, Mg, Fe, Si, and Se, the impurities did not remain in solution despite repeated trials, and despite the use of GaSe to introduce the Se. For Al, Fe, and Si, which are not volatile, the results imply that either their room temperature solubility is below about 10 ppm, or else it is possible that the impurities might have formed oxides, as has been encountered for impurities in copper.[13]

The outstanding feature of Table I is the lack of regularity in the effect of impurities with respect to their position in the periodic table.[14] The large value for Tl, and the order of magnitude difference between Cu and Ag are surprising. The measurements on the latter two impurities were carried out in duplicate to corroborate the results. While these results are not understood, gallium has two properties that differentiate it from metals such as copper, silver, gold, and aluminum. First, it has an orthorhombic structure instead of face-centered cubic, and second, all reported elements have a solid solubility in gallium below 1% by weight with the exception of silver, which has a solubility of only 2%.[15] Finally, because of the small doping concentrations used, the results in general serve to delineate the problem, rather than to be definitive.

IV. CONCLUSIONS

From the variation of resistivity with wire diameter, the mean free path of conduction electrons in high-purity gallium at 4.2°K was determined to be 1.2 mm, at a resistivity of 3×10^{-22} esu. This indicates that the effective number of free electrons per atom in gallium is 0.2.

Each of the quantities in Eq. (1) have been determined for gallium. The effect of scattering from grain boundaries and from effects of induced strains was shown to be negligible in this work. From the temperature variation of resistivity, the value of R_L^* was determined to be 0.4 along the b-axis. From the variation of resistivity with wire diameter, the value of R_S^* was found to be 1.5 for a 1-mm diameter, so that diffuse surface scattering is an important contribution to the residual resistivity in such wires of high-purity gallium. The sum of R_L^* and R_S^*, namely 1.9, is the residual resistivity ratio of a 1-mm diameter wire of gallium in the absence of all impurities. Most of the impurities were found from doping experiments to increase the value of R^* by 0.1 to 1 unit for each atomic ppm. This indicates that residual resistivity measurements on gallium can detect the presence of most impurities at or below levels of 1 atomic ppm.

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[12] A. N. Friedman and S. H. Koenig, IBM Journal 4, 158 (1960).

[13] J. K. Redman *et al.*, Bull. Am. Phys. Soc. 4, 150 (1959).

[14] Compare, for example, the results of C. R. Vassel, J. Phys. Chem. Solids **7**, 90 (1958), for the case of aluminum, which might be expected to be similar to gallium.

[15] M. Hansen, *Constitution of Binary Alloys* (McGraw Hill Book Company, Inc., New York, 1958).