

The second-order terms have been found to be<sup>28</sup>

$$\bar{J}_2 = m^{-3} \int_0^t d\tau (\frac{1}{2}\tau^2) [c\mathcal{A}_2 + c^2\mathcal{B}_2] \Phi(t-\tau), \quad (B3)$$

where  $\mathcal{A}_2$  and  $\mathcal{B}_2$  are defined as follows:

If one designates

$$\theta_1 \equiv \text{div}_{\mathbf{p}_1} \mathbf{p}_1; \quad \theta_2 \equiv \nabla_{\mathbf{p}_1}^2; \quad \theta_3 \equiv (5m\beta^{-1} + p_1^2), \quad (B4)$$

then  $\mathcal{A}_2$  and  $\mathcal{B}_2$  can be expressed as

$$\begin{aligned} \mathcal{A}_2 = & \chi(4)[\theta_1\theta_3] + \frac{2}{3}\eta(4,xx)[2\theta_2\theta_3 + 4\theta_1^2 - 5\theta_1] \\ & + \chi(2,xy; 2,xy)[3\theta_2\theta_3 - 3m\beta^{-1}\theta_2 + 3\theta_1^2 - \theta_1] \\ & + \chi(2,xx; 2,xx)[3m\beta^{-1}\theta_2 + 3\theta_1^2 + \theta_1] \\ & + m^2\Psi(4,xx)[7\theta_2\theta_1 - 24\theta_2] - m^2\Psi(4,xy,xy)[2\theta_1\theta_2] \\ & + m^2\mu(4,x)\theta_2^2 \quad (B5) \end{aligned}$$

and

$$\mathcal{B}_2 = \chi(4)_3[3\theta_1^2] + m^2\Psi(4)_3[6\theta_2\theta_1] - 3\theta_2 \\ + m^2\mu(4)_3[3\theta_2^2] - m[\chi(2)\theta_1 + m\eta(2)\theta_2]^2. \quad (B6)$$

The system constants appearing in the above ex-

<sup>28</sup> Details of the methods of reduction to integrals of this type may be found elsewhere (cf., footnote 22).

pressions have the following definitions:

$$\begin{aligned} \chi(2,xy; 2,xy) & \equiv \int d\xi g_2(\xi) \left[ \frac{\partial^2 \phi(\xi)}{\partial \xi_x \partial \xi_y} \right]^2 \\ \chi(2,xx; 2,xx) & \equiv \int d\xi g_2(\xi) \left[ \frac{\partial^2 \phi(\xi)}{\partial \xi_x^2} \right]^2 \\ \Psi(4; xx) & \equiv \int d\xi g_2(\xi) \frac{\partial^2 \phi}{\partial \xi_x^2} [F_x(\xi)]^2 \\ \Psi(4,xy; 4,xy) & \equiv \int d\xi g_2(\xi) \frac{\partial^2 \phi}{\partial \xi_x^2} [F_y(\xi)]^2 \quad (B7) \\ \mu(4,x) & \equiv \int d\xi g_2(\xi) [F_x(\xi)]^4 \\ \Psi(4)_3 & \equiv \int d\xi_2 d\xi_3 g_3(\xi_2, \xi_3) \frac{\partial^2 \phi(\xi_2)}{\partial \xi_{2x}^2} [F_x(\xi_3)]^2 \\ \mu(4)_3 & \equiv \int d\xi_2 d\xi_3 g_3(\xi_2, \xi_3) [F_x(\xi_2)]^2 [F_x(\xi_3)]^2, \end{aligned}$$

and  $\eta(2)$ ,  $\chi(2)$ ,  $\chi(4)$ ,  $\eta(4,xx)$ ,  $\chi(4)_3$  are defined in the text above by Eqs. (2.32), (2.33), and (3.19).

### Hall Coefficients of Liquid Metals\*†

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The Hall coefficients  $R$  of 9 liquid metals were accurately measured using an alternating-current-alternating-magnetic-field method. Four of these metals have  $R=R_0 \equiv 1/nec$ , which is the value predicted by the free-electron model of liquid metals. The Hall coefficients of these metals (in units of  $10^{-6}$  cm<sup>2</sup>/C) are Hg,  $-7.6$ ; Cd,  $-7.2$ ; Zn,  $-5.2$ ; and Sn,  $-4.4$ . The other five metals were found to have  $R/R_0 < 1$ , with Ga,  $-3.83$ ; In,  $-5.3$ ; Tl,  $-4.8$ ; Pb,  $-3.7$ ; and Bi,  $-3.0$ . The absolute experimental error for Ga is  $\pm 2.5\%$ . The experimental error for all other metals relative to Ga is approximately  $\pm 1.5\%$  except for Pb ( $\pm 12\%$ ). The free-electron model of liquid metals is discussed. The value of  $R/R_0$  is compared with the magnitude of the mean free path. Comparison is also made with the Hall coefficients of other allotropic forms of these metals.

#### INTRODUCTION

ONE of the best means for gaining information about the electronic properties of liquid metals is the measurement of the Hall coefficient. The importance of the Hall coefficient  $R$  lies in the fact that the free-electron theory predicts Hall coefficients equal to the free-electron value  $R_0 \equiv 1/nec$ , where  $n$  is the concentration of valence electrons. A careful study of the devia-

tions of the Hall coefficient from  $R_0$  is therefore a sensitive tool for testing the validity of the assumptions underlying the free-electron theory.

Early attempts to measure the Hall coefficient of liquid metals failed because of magnetohydrodynamic circulating currents and secondary thermal effects, as well as insensitive detecting equipment. In measurements of the Hall coefficient of Hg, for example, des Coudres<sup>1</sup> in 1901 found a nonzero Hall coefficient, but two subsequent workers in<sup>2</sup> 1914 and<sup>3</sup> 1931 failed to find any measurable Hall coefficient. Indeed, until 1960

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<sup>1</sup> T. des Coudres, *Physik. Z.* **2**, 586 (1901).

<sup>2</sup> W. N. Fenninger, *Phil. Mag.* **27**, 109 (1914).

<sup>3</sup> J. Kikoin and I. Fakidow, *Z. Physik* **71**, 393 (1931).

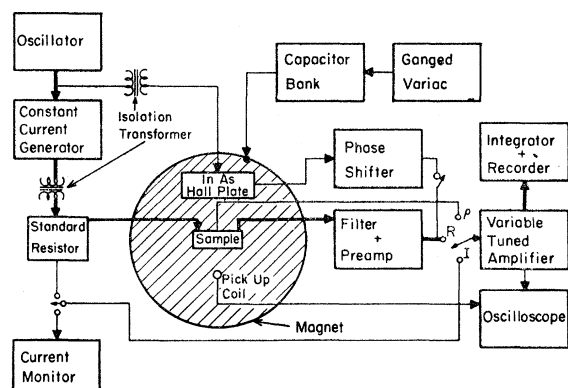


FIG. 1. Block diagram of electronic circuit. An alternating current and an alternating magnetic field at different frequencies produce a Hall voltage which is measured by means of a tuned-amplifier system (also used for measuring the resistivity  $\rho$  and current  $I$ ). The sign of the Hall coefficient was determined by a phase comparison with the signal from an InAs Hall plate.

there was some doubt as to the existence of a nonzero Hall coefficient in liquid Hg.

Recently there has been renewed interest in liquid metals and the Hall coefficient has been successfully measured by several workers. Cusack and Kendall<sup>4</sup> were the first to find that  $R=R_0$  for liquid Hg. They suggested that the free-electron value of the Hall coefficient in liquid Hg might plausibly be attributed to a spherical Fermi surface and isotropic relaxation time in liquid metals generally. Further measurements<sup>5-11</sup> seemed to confirm this suggestion. Hall coefficients of about 10 other liquid metals were also found to agree with their respective free-electron values, apart from possible doubt about Pb and Bi, as noted by Tièche,<sup>10</sup> who has made the most extensive measurements, and later by Enderby.<sup>11</sup> Cusack has summarized the experimental and theoretical developments on liquid metals in an excellent review article.<sup>12</sup> He states: "The general conclusion from Hall measurements on pure metals is that . . . liquid metals behave, galvanomagnetically at any rate, as free electron substances." This conclusion has been generally accepted.<sup>6,8,10,11,13</sup>

However, both because of large experimental errors and because of discrepancies between the results of different workers (see Table I), we felt that the important question of whether or not  $R=R_0$  for liquid metals had not been answered. The aim of the present

<sup>4</sup> N. Cusack and P. Kendall, *Phil. Mag.* **5**, 100 (1960); **6**, 419 (1961).

<sup>5</sup> Y. Tièche, *Helv. Phys. Acta* **33**, 963 (1960).

<sup>6</sup> S. Takeuchi and H. Endo, *Trans. Jap. Inst. Metals* **2**, 243 (1961).

<sup>7</sup> E. G. Wilson, *Phil. Mag.* **7**, 989 (1962).

<sup>8</sup> N. E. Cusack, P. W. Kendall, and A. S. Marwaha, *Phil. Mag.* **7**, 1745 (1962).

<sup>9</sup> G. Busch and Y. Tièche, *Helv. Phys. Acta* **35**, 273 (1962).

<sup>10</sup> Y. Tièche, *Physik Kondensierten Materie* **1**, 78 (1963).

<sup>11</sup> J. Enderby, *Proc. Phys. Soc. (London)* **81**, 772 (1963).

<sup>12</sup> N. E. Cusack, *Rept. Progr. Phys.* **26**, 361 (1963).

<sup>13</sup> C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, *Phil. Mag.* **7**, 865 (1962).

set of measurements is to determine whether any deviation of the Hall coefficient from the free-electron value can be detected by reducing the experimental error. In the following, we report measurements of the Hall coefficient  $R$  of seven liquid metals with an accuracy of approximately  $\pm 1.5\%$  relative to  $R$  of Ga, which was determined with an absolute accuracy of  $\pm 2.5\%$ . This accuracy enables us to establish to within a very small experimental error, that  $R/R_0$  deviates from unity for five metals, and that  $R=R_0$  for the other four metals studied.

In the following section, the contributions to the relative error are carefully segregated from the systematic error. The experimental details are included in this section. The discussion section has two parts. First, we discuss how a short mean free path casts doubt on certain assumptions of the free-electron model. Next, the correlation of the Hall coefficient measurements with the mean free path is discussed. In the Appendix we compare our results with other types of experiments.

## EXPERIMENTAL DETAILS AND ERROR ANALYSIS

### Electronics

The Hall coefficient was measured using an alternating magnetic field  $B$  and an alternating current  $I$  of two different frequencies, the Hall voltage being measured at the sum and difference frequency. This method, first described by Russel and Wahlig,<sup>14</sup> has two distinct advantages. First, since the Hall signal is detected at the sum or difference frequency, the relatively large signals due to other effects appear at different frequencies and can be strongly filtered. A second advantage is that thermoelectric and thermomagnetic gradients cannot follow the external fields even for the low audio frequencies used.

A block diagram of the electronic circuit used is shown in Fig. 1. Power considerations dictate the use of 60 cps for the magnetic field. By neutralizing the inductance with a bank of capacitors, magnetic fields up to 1400 G could be obtained. To prevent errors from magneto-hydrodynamic circulating currents, the magnetic field was made as homogeneous as possible by using a pair of Helmholtz coils. The measured homogeneity was better than one part in  $10^4$  over a length more than twice that of the sample. The magnitude of the magnetic field was determined by measuring the voltage on a pickup coil surrounding the sample. The total absolute error in measuring the magnitude of  $B$  is estimated to be  $\pm 0.3\%$ , of which the relative error is  $\pm 0.1\%$ .

A current frequency of 77 cps was chosen to minimize the noise level at the sum and difference between the current frequency and the 60-cps magnetic-field frequency. All metals were measured at both the sum and difference frequency. Both measurements yielded the

<sup>14</sup> B. R. Russel and C. Wahlig, *Rev. Sci. Instr.* **21**, 1028 (1950).

TABLE I. Measured Hall coefficients.

Metal	Free <sup>a</sup> electron value= $R_0$ ( $10^{-5}$ cm <sup>3</sup> /C)	Measured value= $R$ ( $10^{-5}$ cm <sup>3</sup> /C)	$R/R_0$	$\pm$ Absolute error (%)	$\pm$ Error relative to Ga (%)	Temp. range (°C)	Measured by	Reference <sup>b</sup>
Hg	-7.68	-7.6	0.99		1.4	30-210	Greenfield	P
		-7.46	0.96	4.		(-30)-100	Cusack and Kendall	4
		-7.3	0.96	7.		20-300	Tièche	5
		-9.3	1.22	10.		20-200	Wilson	7
		-8.0	1.04	10.		20	Enderby	11
Cd	-7.29	-7.2	0.99		1.2	321-400	Greenfield	P
		-7.1	0.98	10-15		320-500	Busch and Tièche	9, 10
		-7.0	0.96	10.		321-420	Takeuchi and Endo	6
		-7.6	1.04	4.		321-650	Enderby	11
Zn	-5.12	-5.2	1.01		1.6	420-500	Greenfield	P
		-4.3	0.88 <sup>c</sup>	10-15		422	Busch and Tièche	9, 10
		-5.7	1.16 <sup>c</sup>			600	Enderby	11
		-5.2	1.06 <sup>c</sup>	4.		420-650	Enderby	11
Tl	-6.30	-4.8	0.76		1.4	320-450	Greenfield	P
In	-5.69	-5.3	0.93		1.3	156-320	Greenfield	P
		-5.5	0.98	10.		156-350	Takeuchi and Endo	6
		-5.9	1.05	5.		156-500	Enderby	11
		-4.5	0.80	10.		175-205	Wilson	7
Ga	-3.95	-3.83	0.97	2.5		35	Greenfield	P
		-3.8	0.96	8.		35-110	Cusack <i>et al.</i>	8
		-3.9	0.99	10-15		30-600	Busch and Tièche	9,10
Pb	-5.12	-3.7	0.72	15.		340-500	Greenfield	P
		-1.9	0.38	10-15		400-600	Busch and Tièche	9, 10
		-4.4	0.88	7.		330-550	Enderby	11
Sn	-4.42	-4.4	1.00		1.7	250-320	Greenfield	P
		-4.8	1.07	11.		250-310	Wilson	7
		-4.4	0.98	10.		230-425	Takeuchi and Endo	6
Ge	-3.40	-3.6	1.06	10-15		960-1010	Busch and Tièche	9, 10
Bi	-4.32	-3.0	0.69		2.1	285-330	Greenfield	P
		-4.1	0.95	10.		271-425	Takeuchi and Endo	6
		-2.6	0.60	10-15		271-800	Busch and Tièche	9, 10
Sb	-3.87	-4.4	1.14	10-15		630-980	Busch and Tièche	9, 10
Na	-25.6	-25.	0.98	10-15		98	Busch and Tièche	9, 10

<sup>a</sup>  $R_0$  was calculated using the density at the average temperature of our measurements, with the exception of Hg, for which  $R_0$  is calculated at 30°C. Measured values of  $R$  were, in all cases, adjusted to correct for density variation at temperatures different from the average.

<sup>b</sup> P denotes present work. Numbers correspond to reference numbers in the text.

<sup>c</sup> These values would be 5% lower if our choice of density were used in calculating  $R_0$ . See Ref. 19 of text.

same Hall coefficient. Measurements using other current frequencies such as 70 and 95 cps also confirmed the frequency independence of the Hall coefficient. The current was calibrated using a standard ( $0.01 \pm 0.1\%$ )  $\Omega$  resistor. Since the voltage on the standard resistor and the Hall voltage were both measured on the same tuned amplifier and recorder, only the error of the ratio of Hall voltage to current entered the experimental results.

The measured Hall voltages ranged from  $1.2 \times 10^{-8}$  to  $1.2 \times 10^{-7}$  V. A 60-cps twin- $T$  filter between the high-gain transformer input and the first tube prevented intermodulation distortion. Otherwise, this distortion would occur because of the relatively large voltages at the frequency of the magnetic field and current which arise from pickup and misalignment of the Hall elec-

trodes. The signal was further amplified with a commercial tuned amplifier having a frequency-independent band width of 6 cycles, and then integrated and recorded. The tuned amplifier has a lock-in device which prevents errors from slight frequency drifts. The uncertainty of the gain calibration was measured to be  $\pm 0.5\%$  of which the relative error is  $\pm 0.1\%$ .

The noise level was 4.0 m $\mu$ V and was reduced by a factor of 10 by integrating and recording the voltages for 2 minutes and averaging. The signal-to-noise ratio varied from 300 to 30 between points taken at high and at low magnetic field and current intensities.

The sign of the Hall coefficient was determined by comparing the phases of Hall voltages from the sample and an InAs Hall plate. Both were supplied with cur-

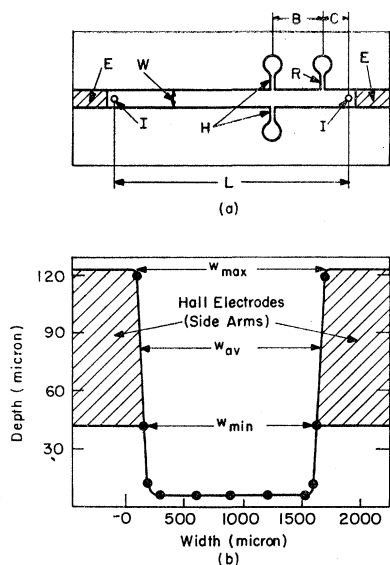


FIG. 2. Cell 2. (a) Top view.  $L=2.00$  cm.  $W=0.145$  cm.  $B=0.481$  cm.  $C=0.208$  cm. Average width of Hall electrodes (H) and resistivity electrodes (R) is 0.020 cm. Average diameter of current electrodes (I) is 0.060 cm. E denotes an epoxy used to fill the ends of the sample groove. (b) Cross section. Note that the depth is expanded by a factor of 50 compared to the width  $w$  (subscripts indicate maximum, average, and minimum).

rent from the same source and situated in the same magnetic field. Using solid copper as a standard, the Hall coefficients measured were found to be negative.

### Sample Cells

The magnitude of the Hall coefficient is sensitive to the precise geometry of the sample cell. For a cell with a rectangular cross section, one can deduce the Hall coefficient from the measured quantities. However, the relative magnitudes of the Hall coefficients of various metals can be obtained from a sample cell with a non-rectangular cross section. Cell 1 was suitable for all temperatures but had a nonrectangular cross section, whereas the cross section of cell 2 closely approximated a rectangle. However, cell 2 could be used only at relatively low temperatures because of the epoxy in its construction. Therefore, we determined the relative values of the Hall coefficients of all the metals very accurately using cell 1 and then fixed the absolute value using cell 2 with Ga.

Cell 2 was drilled to the shape shown in Fig. 2(a). This shape facilitated hand polishing which enabled us to obtain the nearly rectangular cross section indicated in Fig. 2(b). After polishing, an epoxy cement was used to fill the ends of the groove. The depth and shape were determined using a mechanical gauge and a microscope. The relevant parameter is the cross sectional area  $A$  divided by the effective width  $w$ . The quantity  $A/w$  was determined to within an error of  $\pm 0.8\%$ . There is a range of  $\pm 1.5\%$  in the actual width between the elec-

trodes, and we took the effective width to be simply the average width. Measurements of the Hall coefficient of Ga using both cell 1 and cell 2 provided a calibration of the effective ratio  $A/w$  of cell 1 to  $\pm 2.4\%$ .

An over-all view of the sample holder is shown in Fig. 3. The thin plate is clamped by spring loading between the three large plates during a run. The metal was melted in an He atmosphere and by using a slight overpressure, the liquid was gently forced from the reservoir tube into the sample space as well as into the contact wells which are connected with the sample space by means of small side arms (see also Fig. 2). Copper wires, plated with the liquid metal to be measured, made electrical contact with the liquid metal in the contact wells. Thus, sample contamination and contact noise were minimized. It was found necessary to eliminate absorbed gases as much as possible. Therefore, the liquid metals were vibrated overnight at 40 cps in a vacuum at a high temperature. The sample was observed visually during the course of the measurements, and thus it was possible to evacuate and refill the sample cell by means of pressure controls if bubbles began to develop.

The samples were taken from metals of 99.999% purity. Since measurements before and after refilling gave the same Hall coefficient it was concluded that contamination of the liquid metal by the copper electrodes was not a source of error.<sup>15</sup>

The previously described experimental arrangement allowed us to attain a high degree of accuracy as reflected in the following. The Hall voltage was found to vary linearly with magnetic field and current. Figure 4 shows as an example the results for In with the Hall coefficient plotted as a function of current, magnetic field, and temperature as each parameter was successively varied. It should be noted that scatter in the case

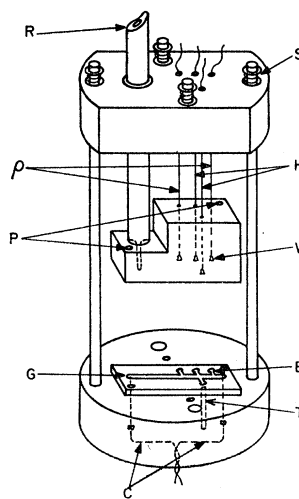


FIG. 3. Over-all view of quartz sample holder. S = spring loading. H = hall voltage electrodes. W = contact wells where liquid metal meets copper electrodes. E = liquid metal electrodes. T = thermocouple. C = current electrodes. G = groove for liquid metal sample. P = holes for aligning pins.  $\rho$  = resistivity electrodes. R = reservoir for liquid metals.

<sup>15</sup> Spectroscopic test of the Ga metal used before and after a run indicated the minute change from 0.0002% to 0.0004% (visual estimate) in the copper impurity concentration.

TABLE II. Density  $D$ , Fermi energy  $E_F$ , resistivity  $\rho$ , relaxation time  $\tau$ , mean free path  $\lambda$ , and related quantities defined in the text  $\lambda/\lambda_{e1}$ ,  $\Delta k/k_F$ , and  $R/R_0$ , for liquid metals.

Group	Metal	Valency	$D$ g/cm <sup>3</sup>	$E_F$ eV	$\rho$ $\mu\Omega\text{-cm}$	$\tau \times 10^{15}$ sec	$\lambda$ Å	$\lambda/\lambda_{e1}$	$\Delta k/k_F$ (%)	$R/R_0$
IA	Na	1	0.929	3.04	9.57	15.3	158.	22.5	0.4	0.98
IIB	Zn	2	6.66	8.96	37.4	0.776	13.9	3.4	2.4	1.01
	Cd	2	8.02	7.06	33.7	1.23	19.3	4.2	1.9	0.99
	Hg	2	13.69	6.85	90.96	0.476	7.39	1.5	5.5	0.99
IIIA	Ga	3	6.10	10.6	25.8	0.871	16.8	4.5	1.7	0.97
	In	3	7.03	8.37	33.1	0.971	16.6	3.9	2.1	0.93
	Tl	3	11.29	7.80	73.1	0.488	8.08	1.8	4.6	0.76
IVA	Ge	4	5.54	11.7	75.	0.26	5.3	1.5	5.2	1.06
	Sn	4	6.97	9.83	48.0	0.524	9.74	2.5	3.2	1.00
	Pb	4	10.60	9.00	95.0	0.304	5.40	1.3	7.3	0.72
VA	Sb	5	6.50	10.7	113.5	0.195	3.78	1.0	8.2	1.14
	Bi	5	10.06	10.0	130.2	0.188	3.54	0.92	9.2	0.69
	%Hg-%In									
	50-50			7.60	40.5	0.911	14.9	3.4		0.88
	75-25			7.26	51.8	0.768	12.3	2.7		0.89
	90-10			6.85	68.6	0.608	9.42	2.0		0.93

of In ( $\pm 0.4\%$ ) was slightly smaller than for some of the other metals. The results of other workers are also shown for comparison. The error from scatter of our experimental points is about  $\pm 0.5\%$  for all metals except Bi ( $\pm 1.2\%$ ) and Pb ( $\pm 15\%$ )<sup>16</sup> to which the following summary does not apply.

The errors in our experiment can be summarized as follows: The total absolute error for Ga is  $\pm 2.5\%$  measured in cell 2. Since we are comparing all measurements to Ga, we find the error relative to Ga by adding the random error of measuring Ga in cell 1 (the cell used for all other metals) to the random error in measuring the other metals. The errors for the other metals relative to Ga range from  $\pm 1.2\%$  to  $\pm 1.7\%$  (see Table I). We emphasize that although the *absolute* error amounts to about  $\pm 4.0\%$  for all these metals except Ga, the important quantity to consider in the discussion of our results will be the much smaller error relative so Ga.

## DISCUSSION

### Free-Electron Model

For polyvalent liquid metals, it is important to examine two of the assumptions on which a free-electron value for the Hall coefficient is predicated. The assumptions in question are (1) the labeling of energy eigenstates by wave number  $\mathbf{k}$  and (2) a collision term in the Boltzmann equation independent of the magnetic field.

It is well known that the solutions of the Schrödinger equation for an electron in a crystal with long-range order can be labeled by wave number  $\mathbf{k}$ . For a liquid,

<sup>16</sup> It is suspected that the large uncertainty in our value for Pb may be due to Pb not wetting the quartz sufficiently well to fill the corners of the cell completely. Another possibility suggested by Tièche is the presence of lead oxide as an impurity. These reasons may also account for the wide discrepancies between the reported values for Pb in the literature, though there seems to be general agreement that the Hall coefficient is lower than the free electron value.

because of the absence of long-range order, one might assume that the electron eigenstates cannot be labeled in such a fashion. Such an assumption, however, is unwarranted since Landau<sup>17</sup> has given an argument to the effect that it is the magnitude of  $\Delta k/k_F$ , which is a measure of the breakdown of such a labeling procedure. Here  $k_F$  is the wave number at the Fermi surface and  $\Delta k$  is the uncertainty in wave number and is related to the mean free path  $\lambda$  by  $\Delta k = 1/\lambda$ . The quantity  $\Delta k/k_F$  is given in Table II for all measured metals. Values were calculated using the indicated densities and resistivities.

A second difficulty arises from the assumption that

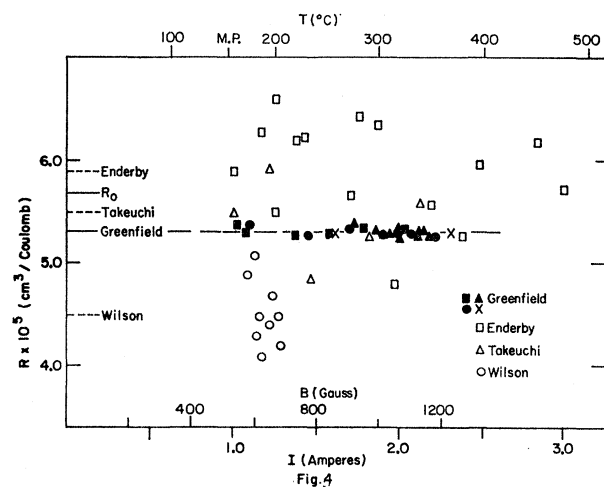


Fig. 4. Our measurement on In of the Hall coefficient  $R$  versus current  $I$  at both the sum (●) and difference frequency (▲), and  $R$  versus magnetic field  $B$  (×) and versus temperature  $T$  (■) at the sum frequency alone. Each parameter was successively varied. For comparison, we have also plotted the Hall coefficient  $R$  as measured by Enderby (□), Takeuchi and Endo (△), and Wilson (○) at various temperatures.

<sup>17</sup> R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, England, 1956), pp. 140-141.

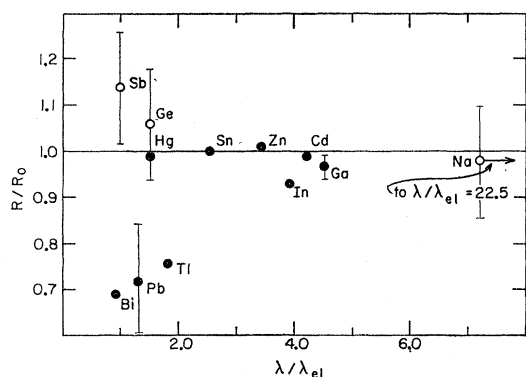


FIG. 5.  $R/R_0$  versus mean free path  $\lambda$  divided by the wavelength of the electron  $\lambda_{e1}$  as calculated from density and resistivity data. The filled circles are values which we measured. The absolute error for Ga is shown. The size of the closed circles indicates the experimental error relative to Ga for all metals except Pb. The open circles were measured by Tièche, and his quoted experimental accuracy of 10 to 15% is indicated as 12% in the figure.

the collision term in the Boltzmann equation used to predict the free-electron value for the Hall coefficient is independent of magnetic field. This assumption is strictly true only for instantaneous collisions. If the time between collisions, which is proportional to the mean free path is not long compared to the time required for the collision process itself, then this assumption begins to break down. Thus, we see that the prediction of the free-electron value for the Hall coefficient of polyvalent liquid metals having electrons with short mean free paths involves several questionable assumptions.

### Discussion of Results

The results and estimated errors of the present work<sup>18</sup> as well as those reported by others are listed in Table I. For Hg, Cd, Zn, and<sup>19</sup> Sn, our experimental values are in agreement with the free-electron value  $R_0$ . For Ga, In, Tl, Pb, and Bi, our measurements show a progressively larger deviation from the free-electron value which, for the latter three, is well outside our experimental error. In addition, Tièche<sup>10</sup> has measured Na, Ge, and Sb, and found that  $R > R_0$  for Sb, but the experimental error of 10 to 15% percent should be further improved before drawing such a conclusion firmly. A plot of  $R/R_0$

<sup>18</sup> Some of the results quoted here are different from those quoted in preliminary reports of our results [A. J. Greenfield, Phys. Letters 3, 121 (1962); Bull. Am. Phys. Soc. 8, 259 (1963)] because of a calibration error in the previous work.

<sup>19</sup> The free electron value for Zn quoted by Enderby (Ref. 11) and Tièche (Ref. 10) is based on a density of 6.92 g/cm<sup>3</sup> at the melting point as given in the *Liquid Metals Handbook*. This handbook claims that this value measured by P. Pascal and A. Jouniaux [Compt. Rend. 158, 414 (1914)] is preferred by the editors of the *International Critical Tables* over that of T. R. Hogness [J. Am. Chem. Soc. 43, 1621 (1921)] who found the density to be 6.59. Smithell's *Metals Reference Book* quotes a recent measurement by E. Pelzel [Bergg. huttenm. Mh. 93, 248 (1948)] who finds a density of 6.66 in close agreement with the measurement of Hogness. In view of this history, it seems more likely that the density of liquid Zn is 6.66, and therefore  $R_0 = 5.09 \times 10^{-5}$  cm<sup>3</sup>/C for Zn at the melting point.

versus  $\lambda/\lambda_{e1}$  is shown in Fig. 5 (see also Table II), where  $\lambda_{e1}$  is the wavelength of the electrons at the Fermi surface. We see that the metals with large  $\lambda/\lambda_{e1}$  (Ga, In, Cd, Zn, and Na) have values for their Hall coefficients close to their free-electron values. On the other hand, the metals with small  $\lambda/\lambda_{e1}$  (Bi, Pb, and Tl, as well as Sb with the above-noted reservation) have deviations of  $R$  from  $R_0$  well outside of experimental error. This pattern is at least qualitatively consistent with the discussion above, which showed why the free-electron model would be expected to become inappropriate when  $\lambda/\lambda_{e1}$  is very small, a possibility that has long been recognized.<sup>12,13,20</sup> When  $\lambda/\lambda_{e1} \lesssim 2$ , our experimental results show that the Hall coefficients display no regularity. Hg and Ge retain the free-electron behavior with  $R = R_0$ , whereas Tl, Pb, and Bi have  $R < R_0$  and, by contrast, Sb has  $R > R_0$ . The different directions of the deviation of  $R$  from  $R_0$  lead us to suggest that there must be at least one other parameter besides  $\lambda/\lambda_{e1}$  which affects the Hall coefficient. In the Appendix, we will summarize the results of the other experiments which complement the above discussion of our results.

In addition, our results have relevance to the known<sup>10,12</sup> similarity of Hall effect and electron diffraction measurements on metal layers deposited at He temperatures. The closeness of the mean free path in the liquid to the mean free path in the deposited layer<sup>21</sup> may be adduced as further evidence that these deposited layers have a liquid-like character. Only for Bi is the Hall coefficient of deposited layers accurately known.<sup>22</sup> Tièche has observed an 11% discrepancy between his measured value for liquid Bi ( $R/R_0 = 0.60$ ) and the deposited layer ( $R/R_0 = 0.67$ ). Considering that  $R$  for solid Bi is several orders of magnitude larger, this could be considered good agreement between the two experiments. Our result for liquid Bi ( $R/R_0 = 0.69$ ), differing by only 3% from the deposited layer result, brings agreement even closer.<sup>23</sup>

### SUMMARY

Hall coefficient measurements form one of the best means of testing the validity of the free-electron model of liquid metals. This model predicts that the Hall coefficient  $R$  is equal to the free-electron value  $R_0 \equiv 1/nec$ . Therefore, careful measurements of the deviation of  $R$  from  $R_0$  are very significant. Of the nine metals we have measured, four metals (Hg, Sn, Zn, and Cd) were found to have no deviation, i.e.,  $R/R_0 = 1$ , and five metals (Ga, In, Tl, Pb, and Bi) were found to have  $R/R_0 < 1$ .

<sup>20</sup> S. F. Edwards, Proc. Roy. Soc. (London) A267, 518 (1962).

<sup>21</sup> W. Buckel and R. Hilsch, Z. Physik 138, 109 (1954).

<sup>22</sup> W. Buckel, Z. Physik 154, 474 (1959).

<sup>23</sup> Deposited layers of Sn do not fit the pattern found for Bi and Ga in that the Hall coefficient [J. Fortmann and W. Buckel Z. Physik 162, 93 (1961)] disagrees with the free-electron value found for the liquid. This is because the deposited layers of Sn were not amorphous enough to justify a comparison with the liquid state, as evidenced by the electron diffraction [W. Ruhl, Z. Physik 138, 121 (1954)] and resistivity data (see Ref. 21).

We find evidence indicating that the length of the mean free path is an important factor governing the extent of free-electron behavior, as might be expected. However, the lack of regularity in the deviation of  $R$  from  $R_0$  when  $\lambda/\lambda_{e1} \leq 2$  lends support to the suggestion that other factors must also play a strong role. One could perhaps determine by means of other experiments whether the unidentified factor is the degree of local order. Another fruitful approach may lie in linking the observed deviations from free-electron behavior with the magnitudes of the pseudopotentials thus providing the basis for a better understanding of liquid metals.

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#### APPENDIX

##### Comparison with Other Types of Experiments

The Hall coefficients<sup>24,25</sup> of liquid Hg-In alloys were found to be less than the free-electron value with a maximum deviation of 13% at a composition of approximately 55% Hg. Figure 6 shows a plot of  $R/R_0$  versus  $\lambda/\lambda_{e1}$ , as calculated from resistivity measurements,<sup>26</sup> and it is interesting to note the shift in behavior from that of increasing deviation of  $R$  from  $R_0$  with decreasing  $\lambda/\lambda_{e1}$ . As the concentration of Hg in the In passes about 50%, some unidentified factor becomes dominant and reverses the trend of this deviation, to the free-electron behavior characteristic of pure Hg. It

<sup>24</sup> N. E. Cusack and P. W. Kendall, *Phil. Mag.* **8**, 157 (1963).

<sup>25</sup> Y. Tièche (private communication).

<sup>26</sup> L. G. Schulz and P. Spiegler, *Trans. Met. Soc. AIME* **215**, 87 (1959).

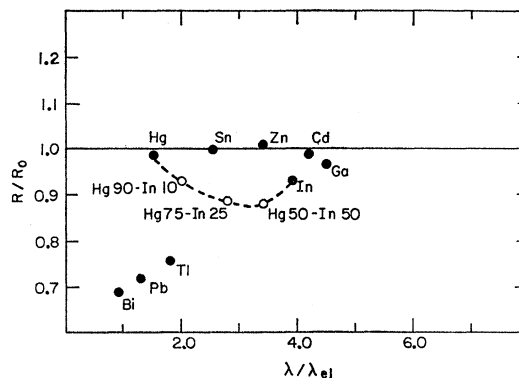


FIG. 6.  $R/R_0$  versus  $\lambda/\lambda_{e1}$  for Hg-In alloys. The increasing deviation of  $R/R_0$  from unity as  $\lambda/\lambda_{e1}$  decreases, characteristic of many metals, is reversed to the free-electron behavior of Hg, as the Hg concentration increases. The open circles are taken from the alloy measurements of Ref. 24.

would be very interesting to measure the Hall coefficient of other alloy systems to determine whether this reversal is particular to Hg or to alloys in general.

A study of the optical properties of liquid metals and alloys also serves to complement our results. The reflectivity and transmission were measured by Schulz<sup>27</sup> with high accuracy for the pure liquid metals<sup>28</sup> Hg and Ga and he finds the free-electron concentration of carriers, which is in agreement with Hall effect measurements. He also measured the reflectivity of the liquid alloys systems Hg-In and Hg-Tl and found that they are definitely not free-electron-like. This is in agreement with the above quoted Hall coefficient measurements of Hg-In. Also, the deviation of the reflectivity from the calculated free-electron behavior was much stronger for Hg-Tl than for Hg-In, again in agreement with our findings of a much stronger deviation of  $R/R_0$  from unity for Tl (24%) than for In (7%).

<sup>27</sup> L. G. Schulz, *J. Opt. Soc. Am.* **47**, 64 (1957); **47**, 70 (1957).

<sup>28</sup> It should be noted that a value for the concentration of carriers for In is commonly, but mistakenly, attributed to Schulz. He never made measurements over a sufficient range of wavelength to determine the concentration [Schulz (private communication)].