Evidence for the Formation of a Pseudogap in a Divalent Liquid Metal

Uzi Even and Joshua Jortner
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel
(Received 12 August 1971)

The Hall coefficient of liquid mercury in the density region 10.0–8.5 gm cm^{-3} exhibits marked density-dependent positive deviations from the free-electron value, providing information on the formation of a pseudogap in a divalent liquid metal.

The classical Wilson-Bloch free-electron model predicts that when the distance a between divalent atoms in a crystalline metal is continuously increased, the overlap between the first and second electronic energy bands decreases, resulting finally in a metal-nonmetal transition. This transition originates from interband overlap effects, rather than from correlation effects.[1] It was suggested by Mott[2] and by Cohen, Fritzche, and Ovshinsky[3] that the gap separating the valence and conduction bands in the expanded solid (or semiconductor) is replaced in a disordered system by a minimum in the density of states, or a pseudogap, in the vicinity of the Fermi energy. Defining a scaling parameter[2] g relating the density of states at the Fermi energy, $N(E_F)$, to the free-electron (FE) value,

$$g = N(E_F)/N(E_F)_{FE}, \tag{1}$$

Mott[2] has predicted that metallic conduction sets in for $g \gtrsim 0.3$. The metallic conductivity σ is characterized[2] in terms of the relation $\sigma = e^2 S_{FE} \Lambda g^2/12\pi\hbar$, where S_{FE} is the free-electron Fermi-surface area and Λ the mean free path. Two metallic conductivity regions can be distinguished[2]:
(a) The weak-scattering region is realized when $\Lambda > a$ and $\Lambda = \Lambda_{FE} g^{-2}$. The conductivity is then given by Ziman's theory[4] and[2] $\sigma > 3000\ \Omega^{-1}\ cm^{-1}$.
(b) The strong-scattering region is realized when $\Lambda \sim a$ so that[2] $\sigma = e^2 S_{FE} a g^2/12\pi^3\hbar$ which is valid for $1 \geq g \gtrsim 0.3$, whereupon[2] $300\ \Omega^{-1}\ cm^{-1} \lesssim \sigma \lesssim 3000\ \Omega^{-1}\ cm^{-1}$. An experimental determination of the density dependence of the g factor in an expanded divalent liquid metal in the strong-scattering region will provide interesting information concerning metal-nonmetal transition in a disordered system originating from band overlap effects. Liquid mercury provides an ideal system for such a study. The wealth of experimental information concerning transport[5-9] and optical[10] properties available for this system is not yet amenable to direct theoretical interpretation. We believe that pertinent information regarding the formation of a pseudogap in the strong-scattering region in this system can be obtained from Hall-effect data. In this note we report the observation in low-density liquid mercury of large, density-dependent positive deviations of the Hall coefficient R from its free-electron value, which provides new insight into the problem of the electronic states of an expanded liquid metal in the strong-scattering metallic region.

It has been realized for some time that the Hall constant for a spherical Fermi surface will depend on the departure of the density of states at the Fermi energy for the FE value.[11,12] Ziman[15] provided a plausibility argument that the ratio R/R_{FE} [where $R_{FE} = (nec)^{-1}$] monitors the ratio of the group velocity of the electron to the current carried by it, wherefore $R/R_{FE} = g^{-1}$ for a nearly free-electron system. It was also pointed out[12] that if the Lorentz force depends on the group velocity of the electron wave packet, rather than on the current, one gets $R/R_{FE} = g^{-2}$. This latter result was derived by Fukuyama, Ebisawa, and Wada[14] for a nearly free-electron system utilizing Kubo's formula. These relations should be applicable for the weak-scattering region. In the strong-scattering region, Straub *et al.*[15a] have provided a theoretical calculation of the Hall conductivity near the metal-nonmetal transition region resulting in

$$R/R_{FE} = g^{-1}. \tag{2}$$

A similar result was recently derived by Friedman[15b] for the strong-scattering region. We shall demonstrate that our Hall-effect data in an expanded divalent liquid metal confirm Eq. (2) in the strong-scattering region, thus providing a measure of the g factor.

We have measured the Hall coefficient of subcritical mercury over the temperature range 20–1475°C (pressure 1–1600 atm). The Hall coefficient was measured by the double ac method. An ac current of ~5 A at 20 kHz and an ac magnetic field of ~100 G at 1 kHz produced a Hall voltage of about $\sim 2 \times 10^{-9}$ V at the sum and at the difference frequencies. The low intensity of the magnetic field, which was homogeneous over the sample volume to better than 0.1%, and the high fre-

quencies employed prevent parasitic signals due to hydrodynamic currents. Extensive (two-stage) passive filtering was employed to prevent intermodulation distortion at the detection system. The total system noise figure was about 6 dB (producing an input equivalent noise of 10^{-10} V after integration of 10 sec). The Hall current was generated by a 20-W power amplifier designed to produce low noise at the difference frequency characterized by a low FM index. The magnetic field was generated by a 3-kW power amplifier, specified by very low total harmonic distortion (0.1%) and FM index. The signal was filtered, amplified by a low-noise filter, filtered again, and detected by a lockin amplifier. A calibration signal (of controlled amplitude and phase) was taken from the Hall current and the magnetic field sources, and injected in series with the Hall-voltage sources, until a null was obtained at the output of the lockin amplifier, thus avoiding frequent calibration checking and reducing the loading of the Hall-voltage source.

The absolute value of $R(T=30°C)$ at room temperature (accounting for the finite sample size[16]) was within 6% of Greenfield's result.[17] Our results in the temperature region 30–300°C are consistent with previous data.[17] Relative values of the Hall signal $[R/R(T=30°C)]$ were obtained to better than 5%. Linearity of the Hall voltage with the magnetic field, the current, and cell thickness were verified. The results were identical upon heating and upon cooling of the cell.

Resistivity of the mercury was measured by the four-probe method at a frequency of 10 Hz, eliminating contact-resistance errors. Values of the relative resistivity (to the room-temperature value) are accurate to within 2%.

The alumina cell of rectangular size of 15×10 mm and relatively high thickness of 0.5 mm was sealed to a long (150-mm) alumina, open-end six-bore tube containing the molybdenum electrodes which do not react with the hot mercury. Sealing of the cell was achieved by a special high-alumina glass frit at 1400°C under high vacuum. The helium leak-tested cell and the long mercury column (150 mm) slowed the dissolution of argon under high hydrostatic pressure into the mercury in the hot zone. The mercury cell was placed in a temperature-controlled furnace (stability of ±0.2°C in the region of 20–1500°C) surrounded by a water-cooled magnet coil, and the whole assembly was placed in an autoclave. The mercury was thus under hydrostatic pressure of compressed high-purity argon. Pressure up to 1600 atm was generated by a two-stage diaphragm compressor, and measured to ±2 atm. Samples were taken from triple-distilled mercury, and the cell was filled under vacuum to eliminate trapped or dissolved gases.

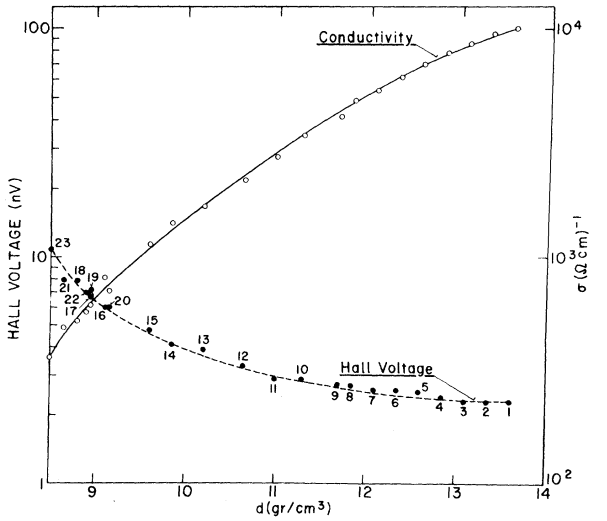

FIG. 1. The density dependence of the electrical conductivity and Hall voltage of liquid mercury. The labeling of the experimental points is given in Table I.

Our experimental results for the Hall effect and for the conductivity of subcritical mercury in the temperature region 20–1450°C (pressure 1–1600 atm) are displayed in Fig. 1 as a function of the liquid density d ($d=13.6$–8.0 g cm^{-3}). The density data were obtained from a recent work of Hensel.[18] Our conductivity data are in general agreement with Hensel and Franck's results,[6] although our measurements exhibit a weaker temperature dependence in the density region $d=9.5$–8.5 g cm^{-3}, than previously reported. The Hall voltage exhibits a linear increase with $1/d$ in the density region 13.6–11.0 g cm^{-3} (20–1000°C) and a much sharper increase at $d=11$ g cm^{-3}. In the lower-density region (high temperature, 1400–1450°C) the Hall voltage seems to be temperature independent (see Figs. 1 and 2). The Hall coefficient (normalized to the FE value) and the Hall mobility $\mu=|R|\sigma$ are displayed in Fig. 2. From these results we conclude the following:

(a) In the density region $d=13.6$–11.0 g cm^{-3} (up to 1000°C) we find that $R/R_{FE}=1$, and $\sigma>3000$ Ω^{-1} cm^{-1}. In this region $\mu\propto\sigma$. This range corresponds to the weak-scattering, nearly free-electron[4] region.

(b) The marked increase of R/R_{FE} in the density region $d=11.0$–8.5 g cm^{-3} is interpreted in terms of the decrease of the density of states

TABLE I. The labeling of the experimental points in the figures.

Point no.	T (°C)	P (atm)
1	35	7
2	100	7
3	200	7
4	300	7
5	400	100
6	500	130
7	600	160
8	700	200
9	800	260
10	900	330
11	1000	420
12	1100	560
13	1200	770
14	1250	900
15	1300	1010
16	1350	1125
17	1375	1235
18	1400	1320
19	1400	1400
20	1400	1500
21	1425	1500
22	1425	1600
23	1450	1600

[Eq. (2)] in the strong-scattering region. In this density range $360 \leq \sigma \leq 2800\ \Omega^{-1}\ \mathrm{cm}^{-1}$ in accord with Mott's prediction[2] for the strong-scattering situation.

(c) In the strong-scattering region $8.5 \leq d \leq 11.0$ g cm^{-3} the electrical conductivity decreases by a numerical factor of ~8, while the Hall coefficient (normalized to the FE value) increases by a numerical factor of ~3 and the Hall mobility decreases by a numerical factor of ~2.5. This behavior is in perfect agreement with Mott's equation[2] $\sigma \propto g^2$ and with the relation[15] $R/R_{FE} = g^{-1}$ [Eq. (2)] whereupon $\mu \propto g$. Thus, Eq. (2) predicts the correct behavior of the Hall coefficient in the strong-scattering region, providing a direct estimate of the g factor. This correlation between the electrical conductivity and the Hall-effect data in an expanded liquid metal in the strong-scattering region concurs with the conclusions of Straub *et al.* on the magnetic-field–induced metal-insulator transition in silicon.[15a]

(d) The lowest g value was experimentally obtained at $d = 8.5$ g cm^{-3} where according to Eq. (2) $g = 0.34$. A bold extrapolation of the experimental data to $g \approx 0.3$ is reached at $d = 8.2$ g cm^{-3} where the electrical conductivity is $\sigma \approx 230\ \Omega^{-1}$ cm^{-1}. This result concurs with Mott's proposal[2] in the strong-scattering limit in liquid mercury (at moderately low density), $\sigma = 2600\ \mathrm{g}^2\ \Omega^{-1}\ \mathrm{cm}^{-1}$, and the limiting value for metallic conductivity is $\sigma \sim 200\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

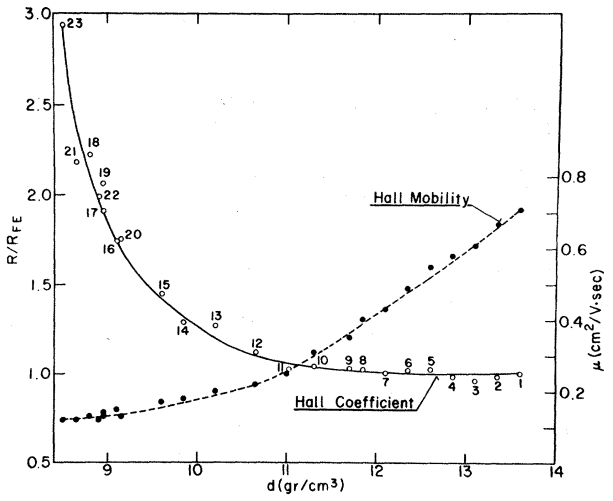

FIG. 2. The density dependence of the Hall coefficient and of the Hall mobility in liquid mercury. The labeling of experimental points is identical to that in Fig. 1.

We are aware of closely related experimental data concerning the Hall effect in metal-ammonia solutions,[19] where insulator-metal transition takes place when the spacing between localized (diamagnetic-spin paired)[20] centers is decreased. Nasby and Thompson[19] recorded $R/R_{FE} = 1$ (i.e., $g = 1$) at high metal concentrations while when the metal concentration is lowered $R/R_{FE} > 1$, a result which can be interpreted in terms of Eq. (2). Unfortunately, at lower metal concentrations the Hall effect of electrolyte solutions[21] sets in, resulting in a maximum in R/R_{FE}, thus obscuring the further increase of R/R_{FE} with decreasing metal concentration, due to the formation of a pseudogap in this system.

We believe that the present results demonstrate the applicability of the Hall-effect data for providing direct evidence concerning the formation of the pseudogap and electron localization in a disordered system. Further work on the Hall effect in subcritical and supercritical mercury is in progress.

We wish to thank Mr. Menahem Levine for his valuable assistance in constructing the electronic equipment and to Mr. Jacob Magen for his expert technical assistance. We are grateful to Dr. F. Hensel for providing us with his unpublished density data. We are indebted to Professor N. F.

Mott, F.R.S., for stimulating comments.

[1]N. F. Mott, Phil. Mag. 6, 287 (1961).
[2]N. F. Mott, Phil. Mag. 13, 989 (1966), and Advan. Phys. 16, 49 (1967), and Phil. Mag. 17, 1259, and 19, 835 (1969).
[3]M. H. Cohen, H. Fritzche, and R. Ovshinsky, Phys. Rev. Lett. 22, 1065 (1969).
[4]N. F. Ziman, Phil. Mag. 6, 1013 (1961).
[5]I. K. Kikoin, A. P. Senchenkov, E. V. Gellman, M. M. Kursunskii, and S. P. Naurazakov, Zh. Eksp. Teor. Fiz. 49, 124 (1965) [Sov. Phys. JETP 22, 89 (1966)].
[6]E. U. Franck and F. Hensel, Phys. Rev. 147, 109 (1966); F. Hensel and E. U. Franck, Rev. Mod. Phys. 40, 697 (1968).
[7]D. R. Postill, R. G. Ross, and N. E. Cusack, Phil. Mag. 17, 519 (1968).
[8]P. Schmutzler and F. Hensel, Phys. Lett. 27A, 587 (1968).
[9]V. Crisp and N. E. Cusack, Phys. Lett. 28A, 712 (1969).
[10]F. Hensel, Phys. Lett. 31A, 88 (1970).
[11]L. Banyai and A. Adela, Phys. Rev. 143, 652 (1965).
[12]J. M. Ziman, *Electrons and Phonons* (Oxford U. Press, Oxford, England, 1960), Chap. 12.
[13]J. M. Ziman, in *Properties of Liquid Metals*, edited by P. D. Adams, H. A. Davis, and S. C. Epstein (Taylor and Francis, London, 1967), p. 551.
[14]H. Fukuyama, H. Ebisawa, and Y. Wada, Progr. Theor. Phys. 42, 494 (1968).
[15a]W. D. Straub, H. Roth, W. Bernard, S. Goldstein, and J. E. Mulhern, Phys. Rev. Lett. 21, 752 (1968).
[15b]L. Friedman, to be published, and private communication.
[16]J. P. Jan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1951), p. 3.
[17]A. J. Greenfield, Phys. Rev. 135, A1589 (1964).
[18]F. Hensel, private communication.
[19]R. D. Nasby and J. C. Thompson, J. Chem. Phys. 49, 969 (1968).
[20]M. H. Cohen and J. C. Thompson, Advan. Phys. 17, 857 (1966).
[21]M. C. Bellisent, P. Gerard, C. Longevialle, M. Menton, M. Pich, and G. Morand, J. Chim. Phys. 68, 355 (1971).

Voltage-Induced Tunneling Conduction in Granular Metals at Low Temperatures

Ping Sheng* and B. Abeles
RCA Laboratories, Princeton, New Jersey 08540
(Received 11 November 1971)

We have observed a new conduction mechanism in granular metals at low temperatures and high electric fields $\mathcal{E}$ characterized by a field-dependent conductivity $\sigma_0 \exp(-\mathcal{E}_0/\mathcal{E})$. A theory based on a simple model of field-induced electron-hole generation in the bulk of the granular metal predicts the observed field dependence and gives expressions for σ_0 and $\mathcal{E}_0$ which are functions of the granular-metal parameters: metal grain size, and thickness and height of the tunneling barriers separating the metal grains. Agreement between theory and experiment is satisfactory.

We have observed a new electronic conduction process at low temperatures in granular metals[1] which consist of fine metallic particles separated by thin insulating tunneling barriers. Unusual transport effects result in these materials from the fact that the electrostatic energy E_c required to transfer an electron between two neutral grains can be appreciably larger than the thermal energy kT. Transport effects in granular metals at high temperatures and low electric fields have been studied by several workers.[2-4] The conduction model proposed by Neugebauer and Webb[2] in this regime is transport of electrons and holes due to tunneling from charged metallic grains to neutral grains, where the density of charged grains is proportional to $\exp(-E_c/kT)$. We have observed a new conduction effect in granular metals in a temperature range where the density of thermally excited charged grains is negligible, and conduction is induced by the application of a large electric field. We show that in this regime the major contribution to the conductivity is due to field-induced tunneling between neutral metal grains separated by one or more barriers.

In this Letter we report the experimental results only for granular Ni. The results for other granular metals (Au and Al) were found to be similar, and will be published subsequently. Granular Ni-SiO_2 films were made by cosputtering from a Ni and a SiO_2 target onto fused-quartz substrates by using the technique of Hanak *et al.*[5] The substrate was maintained at room temperature by water cooling. The relative volume composition x of Ni was determined from thickness measurements.[5] Electron micrography and diffraction showed the specimens to be composed of irregu-