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Interpretation of Transport Measurements in Electronically Conducting Liquids. II. Hall Mobility*

R. S. Allgaier
U. S Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland 20910

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The analysis of transport properties in electronically conducting liquids reported earlier is extended to include the Hall mobility. The experimental relationship between Hall mobility and electrical conductivity is presented and discussed. It is shown that the simple model which was presented earlier to explain the "*n-p* anomaly" can also account for the large difference between the Hall and conductivity mobilities which has been noted in amorphous solids.

This is a brief addendum to an earlier paper which tabulated and discussed the transport properties of a large number of electronically conducting liquids.[1] The earlier paper will hereafter be referred to as ECL. The properties considered in ECL were the electrical conductivity σ, the thermoelectric power α, and the Hall coefficient R.

The present paper deals with a quantity which can be derived from the data tabulated in ECL, viz., the Hall mobility $\mu_H (=R\sigma)$. Values of μ_H and its temperature coefficient are presented in Table I. The entries are arranged as in ECL, i.e., in order of decreasing σ. Figure 1 shows the relationship between μ_H and σ. In almost every case, the data were obtained no more than a few degrees above the melting point of the materials.

Except for a jog in the data between $\sigma = 10^2$ and $10^3\ \Omega^{-1}\text{cm}^{-1}$, μ_H, like the other transport properties discussed in ECL, is a rather smooth function of σ. Furthermore, μ_H is restricted to a remarkably small range of values, considering the enormous σ range covered in Fig. 1.

The smooth evolution of $d|\mu_H|/dT$ as a function of σ reflects the behavior of R and σ in high, intermediate, and low ranges of σ. These ranges were called A, B, and C, and were defined and discussed in detail in ECL.

Range A is the metallic range. The negative $d|\mu_H|/dT$ found there is the consequence of conventional metallic characteristics, a constant R and a negative $d\sigma/dT$. In range B, $d|\mu_H|/dT$ changes sign because R remains constant, or nearly so, while $d\sigma/dT$ becomes positive. However, for those six materials in range B which constitute the mobility anomaly mentioned above, $d|\mu_H|/dT$ is zero or negative. This apparent anomaly in both μ_H and its temperature derivative deserves further investigation. In range C, $d\sigma/dT$ remains positive while dR/dT becomes negative. Both in fact become exponential functions of $1/T$ which are reciprocally related, so that μ_H becomes a constant.

One reason for publishing this paper was simply to remedy the omission of a fundamental transport parameter μ_H from ECL. But in addition, carrier mobilities in noncrystalline material have received considerable attention recently, especially in the case of amorphous solids.[2-8]

The particular problem has been to understand why measured Hall mobilities are of the order of $10^{-1}\ \text{cm}^2/\text{V sec}$ or less,[3,8-11] while the observed behavior of the electrical conductivity, as well as theoretical estimates, suggest that the mobilities of the carriers which dominate the conduction process are in the neighborhood of $10^2\ \text{cm}^2/\text{V sec}$.[3,5-6,8,11-13]

The main point to be made in this paper is that the model presented in ECL leads naturally to a straightforward explanation for this type of mobility discrepancy.

The recent discussions of the mobility problem have dealt with experimental results on amorphous *solids*, while the subject of ECL was *liquids*. However, both kinds of amorphous systems exhibit a persistent, common feature, the "*n-p* anomaly," i.e., the Hall coefficient is negative while the thermoelectric power is positive.[1,3,5,9,14]

The main thrust of the arguments presented in ECL was that the peculiar *n-p* combination was not

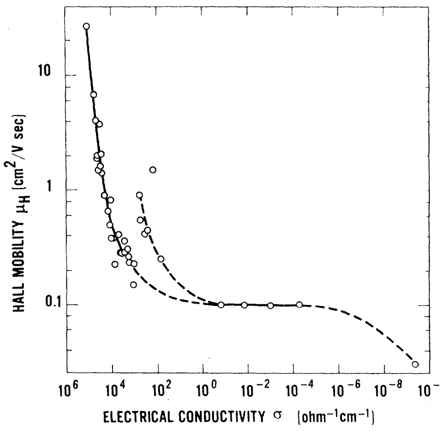

FIG. 1. Hall mobility μ_H versus electrical conductivity σ for the electronically conducting liquids from Ref. 1.

an anomaly and that it could be described in terms of a very simple model. It was also argued that the model was a plausible one for liquids in range B, i.e., liquids in which the negative R corresponded to metallic carrier densities while the behavior of σ and α resembled that in a p-type semiconductor with a positive $d\rho/dT$.

One version of this model is shown in Fig. 2. The left half of the figure shows an energy-momentum ($\mathcal{E}$-p) curve of conventional shape, with a Fermi energy near the top of the band, representing electronic behavior in a valence band. But the constant-energy surfaces remain convex at all band energies, as suggested in the right half of the figure. For simplicity, we assume that the model is perfectly isotropic, i.e., the $\mathcal{E}$-p curves are the same in all p directions and the Fermi surface at every $\mathcal{E}$ is a sphere enclosing electrons.

It is an inevitable consequence of this model that μ_H will be much less than the mobility involved in the conductivity formula. Arguments will be outlined below; to make them convincing, however, it is necessary to approach the task from a point of view which is distinctly different from that normally used to explain transport properties in crystalline solids. Developing this unconventional viewpoint was carried out in detail in ECL and will not be repeated here.

One general type of formula for the total conductivity of a system is written in terms of *properties* of carriers at the Fermi surface only. In the Ziman formula, for instance, those properties are the Fermi-surface area and the electronic mean free path.[15] The second general type is the familiar formula which contains the total carrier density and an average carrier mobility $\bar{\mu}$. It expresses the total conductivities as the sum of the *conductivities* of the individual carriers.

For a partially filled band, the second kind of formula may be written in two ways:

$$\sigma = ne_- \bar{\mu}_n \quad \text{or} \quad \sigma = pe_+ \bar{\mu}_p \quad . \tag{1}$$

In the case of crystalline solids, it is, of course, more convenient and useful to employ the first or second form when the band is nearly empty or nearly full, respectively. It is worth emphasizing, however, that the first form is more fundamental. Whether a material is n or p type, solid or liquid, crystalline or amorphous, σ is always due entirely

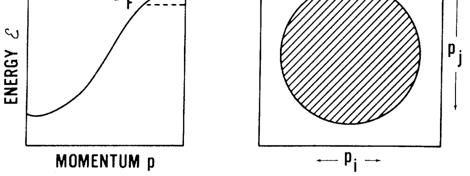

FIG. 2. Simple "n-p" model: (a) energy-momentum ($\mathcal{E}$-p) relation; (b) Fermi surface.

TABLE I. Hall mobilities in electronically conducting liquids.

Liquid	$\lvert\mu_H\rvert$ (cm^2/V sec)	Sign of $d\lvert\mu_H\rvert/dT$	References[a]
Na	26	–	
Ag	7.1	–	
Cu	4.1	–	
Rb	1.9		
Al	2.0	–	
Ga	1.5	–	
Au	3.8	–	
In	1.6	–	
Cd	2.1	~0	
Zn	1.4	~0	
Sn	0.92	–	
Tl	0.66	–	
Ge	0.50	–	b
Hg	0.84	–	
Pb	0.39	–	
InSb	0.5	–	b
Sb	0.39	–	
Bi	0.23	–	
CdSb	0.42	+	
ZnSb	0.28	+	
$AuTe_2$	0.28	+	
GeTe	0.36		b
Bi_2Te_3	0.29	+	b
CuTe	0.31	+	
Sb_2Te_3	0.26	+	b
Te	0.23	+	b
SnTe	0.22	+	b
PbTe	0.15		b
$Te_{92}Sb_8$	0.23	+	
AgTe	0.9	–	c
$Tl_{68}Te_{32}$	0.55	–	c
TlTe	0.42	0	c, d
Tl_3Te_2	0.45	0	c, d
Ag_2Te	15	–	e
Tl_2Te	0.25		c
As_2SeTe_2	0.1	0	
$As_2Tl_2Se_3Te$	0.1	–, +[f]	
$AsTlSe_2$	0.1	0	
As_2Se_2Te	0.1	0	
Se	0.03	+	b

[a] Only references not already given in Ref. 1 are listed.

[b] V. M. Glazov, S. N. Chizhevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Nauka, Moscow, 1967; English translation, revised edition, Plenum, New York, 1969).

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[f] Changes with increasing temperature.

to the electrons present.

In the case of the model shown in Fig. 2 and described above, the constant-energy surfaces remain convex near the top of the band, so that the Hall coefficient measures the density of electrons present, not the density of holes. Hence $R = 1/ne$, not $1/pe$, and $\mu_H = R\sigma = \bar{\mu}_n$, not $\bar{\mu}_p$. According to Eq. (1), $n\,|\,\bar{\mu}_n\,| = p\,|\,\bar{\mu}_p\,|$. Since $n \gg p$, $|\bar{\mu}_n| \ll |\bar{\mu}_p|$.

It is $\bar{\mu}_p$, rather than $\bar{\mu}_n$, which is to be associated with the observed behavior of σ in amorphous solids since it has been analyzed in terms of an intrinsic semiconductor formulation. That is, it refers to small numbers of holes (for which $\bar{\mu} = \bar{\mu}_p$) at the top of a valence band and like numbers of electrons at the bottom of a conduction band having a similar mobility.

Again, it is these much higher *band-edge* mobilities [$\bar{\mu}_p$ (valence band) and $\bar{\mu}_n$ (conduction band)] which are to be identified with the high mobilities obtained from theoretical estimates.[5]

An alternative way to explain the much lower μ_H values makes specific use of the algebraic nature of carrier mobilities. For the model of Fig. 2, it is appropriate to use the formula $\sigma = ne\bar{\mu}_n$ at all Fermi levels, and so n always increases as the Fermi level rises. Consequently, the fact that σ goes to zero at the top of a band requires that $\bar{\mu}_n$ go to zero.

From the point of view of the carriers which are *present*, this is just what happens. The carrier mobility changes sign above the inflection point in the $\mathcal{E}$-p curve of Fig. 2. As the Fermi level rises above this point, $|\bar{\mu}_H|$ decreases in magnitude. Near the top of the band the conductivity due to electrons with normal negative mobilities has been almost completely cancelled by opposing contributions from the electrons with anomalous positive mobilities. Hence at this point, $|\bar{\mu}_n|$ has dropped to a much smaller value than it had in the parabolic region near the bottom of the valence band.

This paper has suggested how a simple single-band model leads to the type of mobility anomaly observed in a number of amorphous solids. Böer has proposed an alternative approach, using a more conventional two-band semiconductor model.[3] There, the lower Hall mobility results from the algebraic cancellation of positive and negative Hall angles of carriers from the valence and conduction bands. There is no corresponding cancellation in the conductivity since the contributions from the two bands in this case add ($e_-\mu_n$ and $e_+\mu_p$ are both positive).

The incredibly simple behavior of μ_H shown in Fig. 1 implies that this quantity is a very fundamental parameter in electronically conducting liquids. Understanding μ_H may offer the best route to a general understanding of the other transport properties. Perhaps this statement will apply to amorphous solids as well.

For example, consider the intermediate and lowest ranges of σ (ranges B and C). In range B, it appears that the observed characteristics may be understood in terms of a metallic nearly free-electron model, despite the behavior of σ and α which earlier had seemed to demonstrate that such liquids were p-type semiconductors. This comment is based on the simple metallic behavior of R which has been found in range B.

In range C, R becomes a very strong function of temperature and rises to enormously larger values than are characteristic of range B. It may be demonstrated ultimately that transport in range C must be described in terms of hopping of carriers between localized electronic states. And yet, the Hall mobilities in these two ranges hardly differ from each other. It seems possible, therefore, that some kind of straightforward extension of the simple model of range B will eventually provide a basis for understanding the behavior in range C also.

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