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Interpretation of Transport Measurements in Electronically Conducting Liquids*

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Measurements of the electrical conductivity σ, the thermoelectric power α, and the Hall coefficient R are tabulated and examined. The properties are found to evolve smoothly as a function of the magnitude of σ, which ranges from 10^5 to $10^{-12}\Omega^{-1}\text{cm}^{-1}$. For $\sigma > 5000$, conventional metallic properties are found. For $\sigma < 100$, the conductivity is due to the hopping of localized electrons. Attention is focused on the intermediate range of σ values, within which σ and α exhibit the characteristics of a p-type semiconductor, with $dp/dT > 0$, while the behavior of R is n type and metallic. A number of problems associated with the semiconductor interpretation are discussed, and it is suggested that the Hall coefficient measurements are more significant than has generally been believed. The traditional procedures by which information about electronic properties have been deduced from transport measurements are carefully reexamined. It is demonstrated that σ and α on one hand, and R on the other, measure different and essentially independent aspects of electronic behavior. The apparently contradictory nature of the data in the intermediate σ range is shown to result from the use of restrictive assumptions and specialized language of the crystalline solid state. A generalized language is developed which can more adequately describe electronic properties in noncrystalline material. Four, rather than two, basic categories of n- and p-type behavior are defined. A simple model is presented which can describe the transport characteristics which predominate in the different ranges of conductivity.

1. INTRODUCTION

During the past twenty years, transport measurements have been carried out on more than 100 different liquids in which the current is primarily electronic rather than ionic. The main purpose of this paper is to discuss the interpretation of the electrical conductivity, thermoelectric power, and Hall coefficient in such liquids. Preliminary reports of portions of this work have been presented elsewhere.[1-4]

Transport measurements are one of the oldest and most common ways of studying the properties of electrons in crystalline solids. Today, they are routinely used to classify crystals as metallic or semiconducting, n or p type, intrinsic or extrinsic, and so on. The behavior of the transport coefficients in many liquids also suggests clear choices between such alternatives. But in recent years, transport data on a growing number of liquids have been published which obviously do not conform to the conventional patterns of behavior found in crystals.

The most commonly occurring anomaly is a conductivity and thermoelectric power which suggest that the liquid is a p-type semiconductor, while the Hall coefficient behavior in the same liquid is characteristic of an n-type metal.[5] Similar results have been found in amorphous solid films[6] and in some chalcogenide glasses.[7,8]

There seem to be two general reactions to this unusual behavior. Some conclude that the complicated nature of noncrystalline systems makes it impossible to interpret transport data in a straightforward manner. Others, noting the experimental difficulties involved in working with liquids, suspect that one of the measurements is unreliable and should be given less weight or disregarded.

This paper presents another alternative. We will argue that much of the confusion and controversy concerning the interpretation of transport measurements in liquids and other noncrystalline systems can be traced to the use of the restrictive assumptions and specialized language of crystalline solid-state physics. We will show that most of the transport data on liquids exhibit remarkably simple and uniform characteristics which are not contradictory and which can be described in terms of a simple plausible model.

However, we will not conclude that all liquids behave in a simple fashion, nor will we argue that such behavior is indicative of the simple nature of liquids. This is not a theoretical paper, and there are many difficult problems concerning the fundamental nature of liquids which will not be discussed here. But we believe that considerable clarification of a very confused situation can be achieved by a careful reevaluation of the experimental data and the procedures by which information about electronic properties is extracted from those data. It is essential to approach the task from a point of view which is appropriate to the nature of the systems being analyzed. That is what we try to accomplish in this paper.

2. EXPERIMENTAL DATA AND SOME GENERAL REMARKS

The transport characteristics to be discussed are summarized in Table I.[9-73] We tried to include only electronically conducting liquids, but it is difficult to be absolutely certain about some of the lower-conductivity liquids. Each entry in the table refers to the lowest temperature at which measurements were made. In almost every case, this temperature was within a few degrees of the melting point of the material.

The column headings in Table I signify the following: σ, electrical conductivity; $d\sigma/dT$, the temperature coefficient of σ; $\sigma_{\min}$, the occurrence (as indicated by a checkmark) of a minimum in the σ-versus-composition curve at the composition listed; α, the thermoelectric power; $d|\alpha|/dT$, the temperature coefficient of the magnitude of α; $R/|R_0|$, the Hall coefficient relative to the magnitude of the free-electron value $[R_0 = 1/n_v N_a e$, where n_v is the number of valence electrons per atom (the average number for binary liquids), N_a is the number of atoms per unit volume, and e is the electronic charge]; and $d|R|/dT$, the temperature coefficient of the magnitude of R.

The liquids in Table I are arranged in order of decreasing σ. In some instances, several σ measurements have been published for a given liquid which do not agree with one another. In such cases, the lowest σ value was used to determine the position of the liquid in the table. This choice was made because we felt that the most likely effect, if any, of contamination or of a deviation from stoichiometry would be to increase σ.

Table I is divided into three parts. Range A covers σ values between 10^5 and 5×10^3 Ω^{-1} cm^{-1}. Most liquids in this range behave in a typically metallic fashion, i.e., they exhibit a negative $d\sigma/dT$, a small value of α, usually negative, which increases with increasing T, and a small negative temperature-independent value of R. These properties are now well understood, thanks to the development of the nearly free-electron model by Ziman[74] and others.

The σ values in part B range from 5000 to 100 Ω^{-1} cm^{-1}. Thus far, most of the liquids which exhibit the unusual combination of p-type semiconducting and n-type metallic behavior lie in this intermediate range.

Range C of Table I includes σ values from 100 down to 10^{-12} Ω^{-1} cm^{-1}. The behavior of σ and α is qualitatively the same in parts B and C of the table. However, recently published measurements suggest that the behavior of the Hall coefficient may turn out to be quite different in the two ranges.[10, 61]

There is a more fundamental reason for separately identifying ranges B and C. The boundary between them is an estimate of the lowest σ value for which it is still possible to describe charge transport in terms of the conventional nonlocalized electronic states. In range C, this traditional framework breaks down and must be replaced by a model in which the conductivity is due to the hopping or tunneling of electrons between localized states.[3]

It has been suggested that this changeover will occur when the mean free path of an electron at the Fermi energy becomes as short as its de Broglie wavelength. The magnitude of σ at this point depends weakly on the carrier density present and on some other factors which have not been precisely evaluated. The value $\sigma = 100$ Ω^{-1} cm^{-1} which we chose lies between two approximate calculations of the boundary value.[2, 75]

The arrangement of the transport data in Table I reveals that, with relatively few exceptions, the properties summarized there evolve in a surprisingly smooth manner as a function of the magnitude of σ. The uniformity of this behavior is illustrated in Table II which identifies the characteristics which predominate in ranges A–C of Table I. The two numbers under each characteristic indicate how many times that type of behavior occurred and how many times a different kind of behavior was found.

The predominating characteristics constitute 87% of 275 measurements from Table I. These figures exclude the Hall coefficient data from range C. At the moment, we are reluctant to identify a predominant behavior on the basis of the available measurements.

3. DETAILED DISCUSSION OF THE DATA

In this section, we examine the conclusions about electronic properties of liquids which others have drawn from transport measurements. A deliberately skeptical point of view will be adopted with regard to previous interpretations of the data. We feel that it is desirable to counterbalance a great deal of casual jumping-to-conclusions which has gone on in the past. For the most part, the discussion is confined to ranges A and B of Table I. Section 6 contains a few remarks specifically directed to the range-C data. References to experimental results are omitted in the course of the discussion when they are readily identifiable from Table I.

A. Electrical Conductivity

The behavior of the electrical conductivity has played a major role in the classification of liquids. It is the most commonly measured transport co-

TABLE I. Transport properties of electronically-conducting liquids.

Liquid	σ ($\Omega^{-1}\mathrm{cm}^{-1}$)	Sign of $d\sigma/dT$	σ minimum	α ($\mu V/°K$)	Sign of $d\lvert\alpha\rvert/dT$	$R/\lvert R_0\rvert$	Sign of $d\lvert R\rvert/dT$	References
				Range A				
Na	104 000	−		−9.9	+	−0.98	0	14, 22
K	77 000	−		−15.5	+			14, 22
GeSi	60 000	−						9
Ag	58 000	−		+10.4		−1.02	0	14, 20, 22
Cu	50 000	−		+16.7		−1.00	0	14, 20, 22
Rb	45 500	−		−7.1	+	−0.7		14, 22, 66
Li	41 700	−		+21.5				14, 22
Al	41 300	−		−2.0	+	−1.00	0	20, 22, 60
Ga	38 800	−		−0.3	+	−0.97	0	14, 22, 45, 60
Mg	36 500	−						22
Au	32 000	−		+3.7		−1.00	0	14, 22
In	30 200	−		−1.0	+	−1.00	0	20, 22, 60
Cd	29 700	~0		+0.5	+	−0.99	0	14, 22, 45, 60
Ge	28 000	−		~0	~0	−1.06	0	14, 22, 33, 41
Cs	27 800	−		+6.4	+			14, 22, 66
Zn	26 700	+		+0.2	+	−1.01	0 +	22, 38, 45, 60
Mn	25 000							22
Sn	20 800	−		−0.5	+	−1.00	0	20, 22, 60
InSb	17 000	−		+0.4	−			35, 41
GaSb	16 000	−		−35	−			14, 21, 41
Tl	13 700	−		−0.5	+	−0.76	0	22, 35, 45, 60
Tl_4As	12 800	−		−16	+			65
Si	12 300	−						22
AlSb	12 000	−						41
Tl_3Sb	11 900	−		−15	+			65
Ni	11 800	−						22
Hg	10 900	−		−3.5	+	−0.99	0	14, 22, 45, 60
Pb	10 500	−		−3.4	+	−0.72	0	14, 22, 45, 60
Co	9 800	−						22
Fe	9 100	−						22
Sb	8 800	−		−0.9	−	−1.14	0	14, 22, 32
Tl_7Sb_2	8 500	−		−22	+			65
Bi	7 800	−		−0.7	+	−0.69	0	14, 22, 45, 60
Ba	7 500							22
Tl_3Bi_5	7 200	−		−19	+			65
$CoTe_2$	6 000	−						55
Ni_3S_2	5 200	−	√	+20	+			28, 30
NiS	5 100	−						31
				Range B				
CdSb	5 000	+	√	~0	~0	−1.5	+	35, 58, 59
ZnSb	4 200 5 200	+		+3	−	−1.2	0	35, 53
Co_4S_3	4 100	−	√					28
$AuTe_2$	3 440	+				−2.1	0	37
Bi_2S_3	3 400	−						31
$CdSnAs_2$	3 200	+						62
GeTe	2 600	+	√	+28	−	−3.6		13, 42, 46
Bi_2Te_3	2 500 2 580 2 800 3 400	+		+4	+	−2.2	+	35, 49, 55, 72

TABLE I. *(continued)*

Liquid	σ (Ω^{-1}cm^{-1})	Sign of $d\sigma/dT$	σ minimum	α ($\mu V/°K$)	Sign of $d\|\alpha\|/dT$	$R/\|R_0\|$	Sign of $d\|R\|/dT$	References
CuTe	1 920 2 200	+		+ 60	0	− 4.0	0	29, 37
Sb_2Te_3	1 800 1 850	+	√	+ 14	−	− 3.9	0	35, 43, 49
Te	1 800	+		+ 20	−	− 3.3	−	14, 25, 35, 67
$NiTe_2$	1 400	−						55
SnTe	1 400	+	√	+ 28	−	− 2.3 − 2.7	+	13, 29, 35, 42, 46
PbTe	1 100 1 500	+	√			− 2.1		13, 42, 55
$Te_{92}Sb_8$	1 050	+				~ − 6	0	13, 14
Bi_2Se_3	900	+		− 35	−			47, 55
Mg_3Bi_2	800		√					54
GaTe	700	+	√					24
$Tl_{68}Te_{32}$	700	+				~ − 15	−	37
HgTe	630	+						55
AgTe	600	+		+ 130	−	~ − 18		29, 37
BiI	590	+		+ 10	−			48, 64
$FeTe_2$	400	+						55
PbSe	400	+						55
FeS	400 1 500	−	√					11, 63
Te_9Se	330	+		+ 50	−			25
TlTe	330	+		+ 110	−			65
Tl_3Te_2	330	+		+ 130	−			65
Cu_2Te	200 500	+	√	+ 100	−			29, 55
Cu_2Se	200	~ 0						55
Ag_2S	200	+	√					28
FeO	180	+						53
Ag_2Te	150	+	√	+ 100	−			29
PbS	110	+						15
				Range C				
Tl_2Te	70	+	√	− 150	−			26, 27
Cu_2S	45 50 60	+	√					17, 28, 63, 69
Te_4Se	40	+						25
CdTe	40	+	√					44
ZnTe	40	+	√					44
Bi_2I_3	39	+		+ 85	−			48, 64
In_2Te_3	25 70	+	√	+ 20	+			23, 71
HgSe	25	+						55
SnS	24 69	+						18, 31
Te_7Se_3	10	+						55
Ga_2Te_3	10 40	+	√					24, 71
Tl_2Se	3.0	+		+ 1540	−			65
Nb_2O_5	2.5	+						57
Sb_2Se_3	~ 2	+	√	~ + 2	−			56
Tl_2Se_3	1.6	+		+ 360	−			65
GeS	1.35	+						52

TABLE I. *(continued)*

Liquid	σ $(\Omega^{-1}\text{cm}^{-1})$	Sign of $d\sigma/dT$	σ minimum	α $(\mu V/°K)$	Sign of $d\lvert\alpha\rvert/dT$	$R/\lvert R_0\rvert$	Sign of $d\lvert R\rvert/dT$	References
MoO_3	1.2	+						12
TlSe	1.1	+		+310	-			65
TeO_2	1.1	+						12
PbO	1.1	+						12
Te_3Se_7	1.0	+						55
CuO	0.4	+						36
InSe	0.3	+		-100	-			68
BiI_3	0.28	+						48
As_2SeTe_2	0.15	+		+500	-	$(-0.6)^a$	-	39, 61
TlS	0.1	+		+580	-			65
Tl_2S_3	1.7×10^{-2}	+		+250	-			65
As_2Se_3-Tl_2Te	1.5×10^{-2}	+				$(-0.5)^a$	-	61
Tl_4S_3	6.5×10^{-3}	+		+1140	-			65
As_2Se_3-Tl_2Se	1×10^{-3}	+				$(-10^2)^a$	-	39, 61
V_2O_5	2×10^{-4} 4.6×10^{-2} 1.6×10^{-2}	+		+				12, 36, 70, 73
Tl_2S	1×10^{-4}	+						55
As_2Se_2Te	5×10^{-5}	+		+850	-	$(-1.3\times10^3)^a$	-	39, 61
Bi_2O_3	5×10^{-5}	+						55
Sb_2S_3	2×10^{-5} 1.5×10^{-2} 2×10^{-1}	+		+				31, 55, 70
Sb_2O_3	1.3×10^{-5}	+						12
Cr_2O_3	6×10^{-6}	+						12
Se	10^{-8} 10^{-7}	+		+800 to +2000	-	$(-3\times10^5)^a$	~0	10, 16, 19, 34, 50, 51
S	$<10^{-12}$	+						40

[a] R, not $R/\lvert R_0\rvert$.

TABLE II. Predominant characteristics of transport measurements on liquids.

Range	Number of liquids	Range of σ values $(\Omega^{-1}\text{cm}^{-1})$	Sign of $d\sigma/dT$	Sign of α	Sign of $d\lvert\alpha\rvert/dT$	R (cm^3/C)	Sign of $d\lvert R\rvert/dT$
A	38	10^5 to 5×10^3	- (34; 2)[a]	- (17; 10)	+ (19; 4)	$\sim 1/n_vN_ae$ (14; 3)	0 (15; 0)
B	34	5×10^3 to 10^2	+ (28; 5)	+ (14; 2)	- (13; 3)	$\sim 1/2N_ae$ (10; 3)	0 or + (8; 2)
C	39	10^2 to 10^{-12}	+ (39; 0)	+ (14; 2)	- (13; 1)	?	?

[a] First and second numbers in the parentheses are the number of times the predominant and a different characteristic were found.

efficient, it is often the first one to be obtained, and in a few cases, it remains the only available measurement. The fact that almost all of the liquids in range B (and, for that matter, all of them in range C) exhibit a positive $d\sigma/dT$ has seemed to many to be strong and convincing evidence that those liquids are semiconductors.

The semiconductor property deduced from the behavior of σ is, of course, that the carrier concentration (intrinsic or extrinsic) increases with increasing T. But σ contains at least two fundamental parameters. In one type of metallic formula, those parameters are the Fermi surface area S_F and the mean free path L_F of carriers at the Fermi level in the expression

$$\sigma = e^2 S_F L_F / 6\pi^2 h, \qquad (1)$$

where e is the electronic charge and h is Planck's constant. Alternatively, the two parameters could be the carrier density n and carrier mobility μ in the familiar expression

$$\sigma = ne\mu. \qquad (2)$$

These two formulas correspond to what might be called the $(\Delta n)\ ev$ and the $ne\ (\Delta v)$ approaches to the calculation of σ. In the first case, σ is computed in terms of *properties* of a slice of displaced carriers at the Fermi level (not from the conductivity of those carriers), while the second form relates σ to the total or the average contribution from all carriers. Some discussions of electrical conductivity are confusing because they indiscriminately jump back and forth between these two viewpoints.

In the case of crystalline solids, most experimental measurements of σ as a function of the temperature T fall into a few recognizable patterns, so that it becomes evident whether a given material is metallic or semiconducting. The choice is made easier by the fact that it is almost always a good approximation to assume that the band structure is temperature-independent. Then σ changes with T only because carriers are thermally redistributed and because their scattering times are temperature-dependent.

On the other hand, the very structure of a liquid often changes significantly with temperature. This can alter the transport model and the carrier properties in a much more general and fundamental way. It becomes quite difficult and risky to use $\sigma(T)$ data on liquids to deduce information about $n(T)$ and $\mu(T)$.

There is, for example, the exceptional behavior of Cd and Zn in range A of Table I. These divalent metals exhibit a zero or slightly positive $d\sigma/dT$ over a considerable temperature interval in the liquid phase. In addition, there are a number of binary alloys of liquid metals (not included in Table I) which behave in a similar fashion over composition ranges which also correspond roughly to an average of two valence electrons per atom.[20, 76]

In terms of conventional models, the explanation for such behavior would have to be that the carrier density rises fast enough with increasing T to completely compensate for the decreasing mobility normally expected. But no one has suggested that Cd and Zn are liquid semiconductors, and ultimately the nearly free-electron model provided a straightforward explanation within the framework of a strictly constant carrier density.[3]

For two carriers per atom, the de Broglie wavelength is strongly interacting with the nearest-neighbor distance. In a liquid this distance is not a single number, but a peaked distribution of values. The width of the peak grows as T increases, weakening the interaction and leading to the nearly constant behavior of $\mu(T)$.

But the above discussion refers to exceptional behavior in a range of σ values which otherwise exhibit metallic characteristics. It might be argued that the positive $d\sigma/dT$ behavior predominates in range B and should be regarded as sufficient evidence to classify the liquids as semiconductors.

There are some problems, however. Why does the change from metallic to semiconductor model occur so smoothly, i.e., over such a narrow range of σ values? After all, the presence of a variety of energy gaps and impurity densities ought to have a randomizing effect on the relation between σ and the other tabulated properties. The over-all behavior is in fact suspiciously uniform and simple for the traditional semiconductor model which can exhibit intrinsic and several varieties of extrinsic behavior.

The simplicity might seem reasonable if impurities become electrically inactive in noncrystalline materials. It has been found that impurities have little effect on σ in certain glasses[77] and in liquid Se.[10, 78]

But when the temperatures of at least six liquids from range B are raised high enough above their melting points, σ stops increasing and, in some cases, starts to decrease again. These characteristics were found in FeO,[53] In_2Te_3,[23] Ga_2Te_3,[24] and in CdSb, ZnSb, and Te,[20] and do not correspond to the normal behavior of intrinsic semiconductors.

Furthermore, the cusplike minima frequently seen in the σ-versus-composition curves for range-B binary liquids (to be discussed in Sec. 3C) demonstrate that the nonstoichiometric kind of self-doping impurity has a very important effect on σ.

Another way of using σ data to argue that a liquid is a semiconductor runs as follows: The conductivity of solid semiconductors is significantly lower than that in metals because of the presence of a substantial energy gap. If σ does not change much when such a material melts, the gap must still be present, and therefore the liquid is also a semiconductor.

This reasoning requires careful examination. First of all, there are some pertinent features in the general behavior of σ in range A. When monovalent metals melt, their conductivities usually drop by about a factor of two.[22] The solid- and liquid-state models which can account for this change in σ might both be described as having a more or less spherical Fermi surface enclosing one carrier per atom. Melting causes the mobility to drop to half its solid-state value, and this change is almost entirely due to a change in the scattering time of the carriers. Hence, it appears that the modest change in σ reflects the fact that melting has very little effect on the band model of a monovalent metal.

But it is also true that σ drops by about a factor of 2 when the polyvalent metals Mg, Zn, Cd, Al, Tl, Sn, and Pb melt.[22] This is a rather startling result, since it seems evident that there must be a profound change in band structure when these metals melt.

In a solid polyvalent metal, the Fermi surface cuts through a number of Brillouin-zone boundaries. When reassembled in the reduced zone scheme, it generally consists of sets of electron and hole pockets. These pockets enclose carrier densities which are not related to the number of valence electrons, and individually they often contain less than one carrier per atom. But the Hall coefficient in the liquid polyvalent metals suggests that there is a single Fermi sphere enclosing 2, 3, 4, or even 5 electrons per atom, i.e., all of the valence electrons.[45]

Hence, on one hand, the behavior of the Hall coefficient suggests that the complicated multiband structure is completely destroyed when the polyvalent metal melts, while at the same time the modest change in σ indicates that very little has happened to the model, just as in the monovalent metals. We will discuss this behavior further in Sec. 4.

When nonmetallic solids melt, the changes in σ are sometimes more substantial, but still they do not reflect the drastic changes in the model which other data suggest have taken place. An extreme example is Bi. When it melts, σ rises, but only by a factor of 2 to 3 (σ is anisotropic in the solid), even though it is known that the carrier concentration jumps from about 10^{17} per cm^3 to 5 carriers per atom, an increase of 5 orders of magnitude. Modest increases in σ are also observed when some 4–6 semiconductors melt, despite evidence from Hall measurements (see Table I) of much more substantial changes.

These examples illustrate how difficult it is to draw conclusions about the nature of liquids from the behavior of a single type of transport measurement. The electrical conductivity seems particularly unsuitable for this purpose. It is very insensitive to the major changes in band structure which frequently occur with melting, and its temperature dependence in the liquid phase can be very misleading.

B. Thermoelectric Power

The usual derivation of the thermoelectric power α for the case of degenerate statistics predicts that it will be inversely proportional to the Fermi energy, and hence relatively small in metals. But because it is small, and sensitive to a number of details of carrier behavior, the magnitude of α varies considerably from one solid metal to the next, and even becomes positive in some metals which are "highly" *n* type (e.g., monovalent metals). So it is not particularly surprising to find considerable scatter and some positive values for α in the liquid phase as well, as shown in range A of Table I. The standard derivation of α in metals also predicts that α will increase with increasing T. This is usually found in solid metals and also in range A of Table I, but again there are some exceptions.

But in range B, the behavior of α changes and becomes more uniform. At the same time that $d\sigma/dT$ changes from negative to positive, α becomes positive and $d|\alpha|/dT$ becomes negative. Thus $\alpha(T)$ seems to confirm the notion that most liquids in range B are semiconductors with increasing carrier densities. Moreover, it suggests that they are *p*-type semiconductors.

But again the results are strangely simple and uniform for a semiconductor model. If the observed behavior is intrinsic, why are practically all of the liquids *p* type, since intrinsic solid semiconductors are usually *n* type? If the liquids are extrinsic semiconductors, is it reasonable to believe that almost every liquid semiconductor thus far studied just happened to be contaminated with donor impurities?

C. Composition Dependence of the Electrical Conductivity and Thermoelectric Power of Binary Liquids

The composition dependence of the transport behavior of liquid alloys has been reported for many pairs of the elements which comprise part A of Table I.[79] Measurements over substantial composition ranges have also been carried out on at least 19 of the binary liquids from parts B and C of the table. The latter series of measurements are particularly interesting because they cover enormous ranges of composition which do not exist as single-phase crystalline solids. Figure 1 summarizes the composition ranges which have been studied.

According to column 4 of Table I, composition studies in ranges B and C have often found that a sharp minimum in σ exists at or near the listed composition. In conventional terms, this behavior suggests that the stoichiometric liquid is a semiconductor and that adding an excess of one component or the other introduces electrons into the conduction band or holes into the valence band of that semiconductor.

In terms of this conventional interpretation, it is strange to note that the σ minimum sometimes shifts to a significantly different composition or fills in and vanishes, or almost vanishes, as T in-

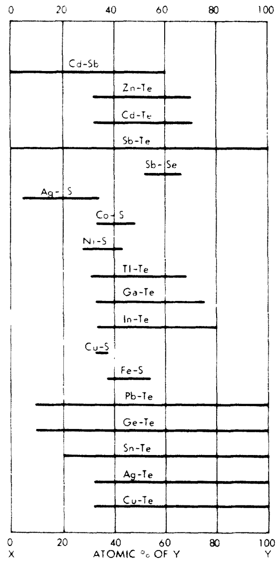

FIG. 1. Compositions of binary liquids from range B of Table I for which transport measurements have been carried out.

creases.[23, 24]

Another problem arises in connection with deciding which direction of nonstoichiometry leads to *n*-type and which to *p*-type behavior in the liquid. The nonmetallic component of almost all of the binary liquids in Table I is one of the chalcogens O, S, Se, or Te. In most cases adding excess metal or excess chalcogen to a solid chalcogenide makes it *n* type or *p* type, respectively. A few of the earliest studies of σ as a function of composition in the liquid simply assumed that the same relationships would hold there also. In some cases, the signs of α which were later found on either side of the stoichiometric liquid were consistent with these assumptions.[26, 29, 30]

But the behavior of the solid chalcogenides is unusual. To make a column-IV semiconductor such as Ge *n* type or *p* type, a column-V or column-V or column-III impurity must be added, i.e., the Fermi level is raised or lowered by increasing or decreasing the average valence of the material. The same rule applies to many metallic alloys in the solid state.

The behavior of most solid chalcogenides is opposite to the above, and this was originally explained on the basis of a vacancy-ion model. For example, Pb and Te in PbTe were regarded as positive and negative ions. Removing Te atoms leaves electrons behind. Hence, lowering the average valence raises the Fermi level, making the solid *n* type.[80]

But there are exceptions: Adding Te to solid Bi_2Te_3 makes it *n* type. The Te is believed to substitute for the Bi in this case.[81] Furthermore, it has been suggested that GeTe may be made *p* type by removing Ge from the Ge sublattice and also by substituting Ge for Te on the Te sublattice.[82] In this solid chalcogenide, it appears that opposite changes in stoichiometry can move the Fermi level in the same direction.

The various effects described above can only be explained consistently by a model which specifies the sublattice on which the vacancies and substitutions occur. But how can such distinctions be carried over to the disordered liquid phase? It would seem most reasonable to conclude that the number of conducting electrons in liquids will reflect the average valence of its constituents. Hence, it is not obvious that the signs of α seen on either side of stoichiometry in most liquid chalcogenides may be interpreted conventionally, simply by analogy with the behavior of the corresponding solids.

More serious objections to the semiconductor interpretation of the composition studies stem from the properties of the binary liquids found at compositions far removed from the stoichiometric formulas listed in Table I.

For example, the Cu-Te, Ag-Te, and Sn-Te systems have been studied all the way from the stoichiometric compositions shown in Table I to pure Te.[29] In each instance, α remains positive throughout the entire composition range, despite the fact that the conventional band-model interpretation suggests that one or more bands are completely emptied in the process. Furthermore, in these same systems, as well as in Pb-Te and Ge-Te,[42] σ increases monotonically between the stoichiometric liquid and pure Te. Since the liquids at both ends of each composition range are supposed to be semiconductors, the conventional picture would predict the occurrence of a maximum σ at some intermediate composition.

Perhaps the most serious problem of all is the temperature dependence of σ and α. Positive values of $d\sigma/dT$ and negative values of $d|\alpha|/dT$ have been found over the ranges of composition which are summarized in Fig. 2.

Adding 10 or 20% excess of one component or the other to the binary liquid should introduce carrier densities of the order of one carrier per atom, according to the conventional band picture. Even at these elevated temperatures, such densities should swamp out the intrinsic carriers of the stoichiometric liquid, and the highly nonstoichiometric liquid should acquire metallic characteristics.

But this does not happen. How can it be argued that the positive $d\sigma/dT$ and the negative $d|\alpha|/dT$ seen in the stoichiometric liquids are a reflection of their semiconducting nature when the same properties are seen over tremendous ranges of composition within which conventional models ought to be metallic?

D. Hall Coefficient

Until recently, almost all of the Hall-coefficient measurements which had been made on liquids

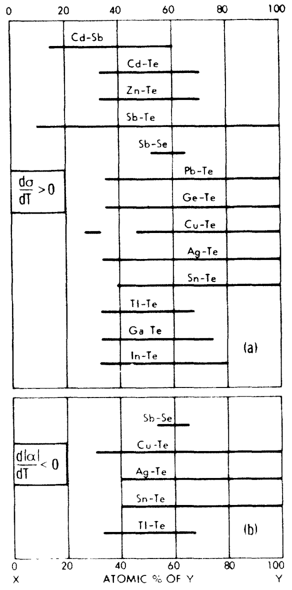

FIG. 2. Compositions of binary liquids from range B of Table I for which (a) $d\sigma/dT$ is positive and (b) $d|\alpha|/dT$ is negative.

were confined to range A. One important exception was a 1957 study of solid and liquid Te. It found that R remained positive and large (between two and three orders of magnitude larger than R_0) when Te melts. With further increase in temperature, R decreased, and finally became negative at 575 °C, more than 100 °C above the melting point.[83]

Thus, at one time, there were Hall measurements which reinforced the conclusion, deduced from the behavior of σ and α, that liquid Te is a p-type semiconductor. In the absence of other data, the Hall measurements on Te have been cited repeatedly as further evidence for the existence of liquid semiconductors. They are very pertinent, since so many of the liquids outside range A contain Te or one of the other chalcogens.

But the 1957 measurements are not shown in Table I. They have been superseded by two newer investigations, both of which found that R immediately becomes negative and small ($n \approx 2$) when Te melts.

Hall measurements have now been reported for at least 12 other liquids from range B. In all of them, R is negative[84] and small, and in most cases $n > 1$ (using $R = 1/nN_a e$) and is not increasing with increasing T.

Not shown in Table I are the Hall measurements on the Tl-Te system which were obtained on a number of compositions between Tl_2Te and $TlTe_2$.[85] The results were always negative, despite the fact that the behavior of σ and α suggests that all compositions in this range are p-type semiconductors with carrier densities which increase with increasing Te content.[27]

In range C, R becomes large and strongly temperature-dependent and hence quite different from range B. Nevertheless, R is negative and α is positive for every liquid from range C on which both measurements were made. And, as mentioned in Sec. 1, this same combination of signs has also been seen in glasses[7,8] and amorphous solid films.[6] In fact, this behavior has been observed often enough to be described as one of the characteristic types of behavior found in noncrystalline systems.

Thus, it has now turned out that the Hall-coefficient behavior in range B is very similar to that in range A. The only general distinction seems to be that in range A, $n = n_v$ (all the valence electrons) while in range B, $n = 1-3$ in most cases. Actually, the average value for the 10 highest-σ liquids in range B is 2.0. Another difference is that some of the Hall data in range B exhibit a modest temperature dependence.

The n-type metallic behavior of R in range-B liquids strongly conflicts with the semiconductor model, based on the σ and α data, which had gradually built up over many years. The contradiction seems particularly strong in at least six cases for which the metallic behavior and the cusplike minima in σ occur at the same compositions. If the semiconductor interpretation is not appropriate at these stoichiometric compositions, can it be expected to apply elsewhere?

Some explanations of the negative R–positive α combination have been proposed for particular materials. For example, it was suggested that the results in the chalcogenide glasses might be due to an n-type crystalline phase dispersed in the p-type glass.[8] But, as noted in Sec. 1, the more usual response has been to view the unusual nature of the transport data with suspicion, ascribing it to inadequacies of the available theories or to experimental difficulties.

It is almost always the Hall coefficient which is regarded as the least significant measurement.[86] This is not surprising since the σ and α data are far more numerous, presumably because they were easier to obtain. There is no doubt that it is very difficult to work with the thin layers of hot liquid needed to generate measurable Hall voltages. Furthermore, throughout most of its long history, the Hall coefficient has not enjoyed a particularly good reputation as a useful and reliable experimental tool.

Fifty years passed before the first problem of the Hall coefficient, the occurrence of positive values in a number of familiar solids, was solved by the quantum-mechanical band theory of solids. In recent years, the problem has been to relate the behavior of R to the various details of the complicated models now known to be appropriate for crystalline solids.

It is rather surprising to find that even slight deviations from the simplest of models transforms the computation of R into an enormously complex and tedious problem. The Hall coefficient, after all, is primarily determined by a single fundamental parameter, charge density. When it is written

$$R = r/nN_a e, \tag{3}$$

all of the complicated influences of band structure on carrier behavior are contained in the dimensionless factor r.

We showed recently that it is a very simple matter to compute r for a Fermi surface which is composed of planar faces.[87] We used this simplicity to develop some general rules for the behavior of r. One conclusion is that r will lie between $\frac{1}{2}$ and 1 (or slightly higher) for a wide variety of one-band models. In other words, the effect of a variable or anisotropic (i.e., nonfree electron) response of a given group of carriers is almost always to reduce their average Hall angle.

Having made these remarks, what can we say in general about the reliability and significance of the Hall data on liquids from ranges A and B? Table I shows that in range A, the values of r are temperature-independent and, in most cases, lie within 2 or 3% of the free-electron value corresponding to all of the valence electrons. This demonstrates, at least for range A, that it is possible to obtain accurate measurements of R which are in accord with other measurements and with theory.

It is also interesting to observe that all measured values of r in range A lie between 0.69 and 1.14. This range is strikingly similar to that expected and found in crystals, and hence it is possible to interpret the results in the same manner, viz., as a measure of the anisotropic response of the electrons.

Greenfield plotted the ratio R/R_0 for range-A liquids as a function of L_F/λ_F, where L_F is the mean free path and λ_F the de Broglie wavelength of electrons at the Fermi level.[45] He found that deviations from unity only occurred when $L_F/\lambda_F \lesssim 2$, but not in all such cases. The deviations were ascribed to the uncertainty in λ_F which becomes comparable to λ_F itself when $L_F/\lambda_F \approx 1$.

But a correlation between r and L_F/λ_F need not occur in all cases if r is primarily a measure of anisotropy. In order for the electrons to respond in a mixed or anisotropic way to the environment, their mean free paths must not be long compared to a parameter which defines the extent of local order. This is a necessary condition, but it is not sufficient to reduce r significantly below unity.

The magnitudes of R/R_0 shown in range B of Table I are, on the whole, less accurate than those in range A. It is more difficult to measure R in range B, and some of the densities of the liquids (from which R_0 is computed) are not as well known. But they are accurate enough to show that all of the valence electrons are not contributing substantially to the conduction process. Enderby and Walsh suggested that some might be in essentially atomiclike states separated from the continuum of conducting electrons.[35] But in any event, the value $n \approx 2$ certainly does not imply that there is anything wrong with the Hall measurements.

It seems firmly established that the Hall coefficient is sometimes temperature-dependent in range-B liquids. In three cases, R increases and then levels off as T increases. Enderby and Walsh noted that this effect might reflect the disappearance of local order.[35] We can add that $r \approx \frac{3}{4}$ at the melting point in these three cases, if it is assumed that the higher-temperature plateau corresponds to $r = 1$. As noted earlier, this is a reasonable value for an anisotropy factor.

The newer Hall data on liquid Te show that R decreases and levels off as T increases. Whether this change corresponds to the generation of additional carriers remains to be seen, but we might note that the high-T limit corresponds to $r = 0.8$, also a reasonable anisotropy factor, if it is assumed that $n = 2$.

The above discussion leads us to conclude that the Hall-coefficient behavior in ranges A and B, when examined on its own merit, is generally reasonable.

4. RELATIONSHIPS BETWEEN TRANSPORT MEASUREMENTS AND ELECTRONIC PROPERTIES

What we have said up to this point about the behavior of transport measurements in range B may be summed up as follows: The characteristics of σ and α are similar to those of a p-type semiconductor with a positive dp/dT, but a number of problems arise from this conventional interpretation. The Hall-coefficient behavior suggests that range-B liquids are n-type metals. If this behavior is accepted on its own merit, then the magnitude and temperature dependence of R are generally reasonable and may be interpreted in a straightforward manner.

Is it inevitable that accepting the one kind of result requires that the other kind be rejected? To answer this question, we must reexamine the traditional procedures by which information about electronic properties is extracted from the characteristics of transport measurements.

We begin by reviewing the manner in which σ evolves as a typical energy band in a crystalline solid is filled with carriers. The description may be simplified, without loss of any essential features, by assuming that the scattering time τ does not change with energy. Then the changes in σ will be due solely to the contributions of the carriers newly added. The new carriers will not affect the contributions to σ from carriers already there, as they would if τ depended on energy and the statistics were degenerate.

A sketch of the relationship between carrier characteristics and the behavior of σ is given in Fig. 3. Four stages in this evolution are identified. At the bottom of the band, the energy-momentum ($\mathcal{E}$-p) relation is parabolic, so that the mobility is constant and σ is proportional to n. In the second range, the band becomes nonparabolic, so that the effective mass increases, μ decreases, and σ increases less rapidly than n.

At the boundary between regions 2 and 3, the effective mass reaches infinity and changes sign. The carriers in region 3 have a mobility which is opposite in sign to that of the carrier charge. Their contribution to the current therefore opposes that from regions 1 and 2, and σ decreases with increasing n. Finally, near the top of the band, there is a second parabolic region within which the effective mass is again constant, but negative. In this range, σ decreases most rapidly, ultimately reaching zero when the contribution from the negative effective-mass carriers just cancels that from the carriers with positive effective masses.

The above was an "$ne(\Delta v)$" type of description, corresponding to Eq. (2). The alternative description, based on Eq. (1), links the behavior of σ to the evolution of the Fermi velocity (the slope of the $\mathcal{E}$-p curve), and leads to the same results.

This familiar behavior was reviewed in detail in order to emphasize the fact that its essential features may be described entirely in terms of the energy dependence of the effective mass or mobility, i.e., in terms of the shape of some average $\mathcal{E}$-p curve.

There was no reference to the form of the Fermi surface. It did not have to change from convex to concave when the conductivity became p type. Nothing prevents the Fermi surface from remaining convex and continuing to grow in area while σ decreases smoothly to zero. To infer from σ data alone that a concave Fermi surface is present has always been an assumption. For crystalline solids it is, of course, a reasonable assumption, since the negative second derivatives of the $\mathcal{E}$-p curves and the concave energy surfaces always appear above a certain energy level in conventional bands.

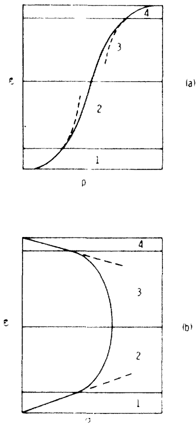

FIG. 3. Simple model to illustrate the relationship between (a) an energy-momentum ($\mathcal{E}$-p) curve and (b), the electrical conductivity σ as a function of $n(\mathcal{E}_F)$, the density of carriers up to the Fermi level.

A transport effect such as σ might be called "one dimensional" or "longitudinal". It is one dimensional in the sense that a single, averaged $\mathcal{E}$-p curve is sufficient to describe the evolution of σ. It is longitudinal in the sense that it relates the current to the components of the applied forces which are along the direction of the current.

The electronic characteristics transverse to the current direction affect σ only slightly, if at all. For instance, a spherical Fermi surface of a given size with a given Fermi velocity and scattering time leads to precisely the same value of σ whether the surface encloses electrons or holes.

The behavior of α is strongly linked to that of σ, so that it too may be regarded as a longitudinal transport coefficient. For example, in a certain class of metallic models, α and σ are related by[88]

$$\alpha = \tfrac{1}{3}\pi^2 (k^2T/e)[\partial \ln\sigma(\mathcal{E})/\partial\mathcal{E}]_{\mathcal{E}=\mathcal{E}_F}, \qquad (4)$$

where k is Boltzmann's constant and $\mathcal{E}_F$ is the Fermi energy. This relation shows that α becomes p type when σ begins to decrease, rather than to increase, with increasing n. In more general terms, we may say that α has the normal or the opposite sign according to whether warmer (more energetic) carriers tend to drift into regions containing cooler (less energetic) carriers, or vice versa.

In any event, α is responding to the way that carrier properties vary with energy, not to the shape of the Fermi surface. This point finally received the attention it deserves in a recent paper by Robinson.[89] He was discussing the old problem of the negative R and positive α values found in solid Cu, Ag, and Au. He noted that all previous attempts to explain this peculiarity had failed because they ascribed the positive α to the partially concave necks of an otherwise conventionally n-type Fermi surface. He pointed out that this feature could hardly be the basis for the positive values since they persist in the liquid state. Robinson then showed that the positive values of α were due to the negative values of $d\sigma/d\mathcal{E}$. The presence of the necks on the Fermi surfaces of the noble metals was ignored completely.

The Hall coefficient, on the other hand, is a "transverse", three-dimensional effect. It depends on the shape of a constant-energy surface, and on the manner in which the electronic properties vary over this surface. It cannot even be described properly in less than three dimensions: two for the longitudinal and transverse forces and currents, and a third to specify the direction of the magnetic field.

Everyone knows that the sign of R is determined by whether carriers are deflected to the right or left in crossed electric and magnetic fields. But it does not seem to be widely appreciated that this behavior is essentially independent of the longitudinal electronic properties, i. e., of the magnitude and sign of the effective mass. Part of the reason may be that textbooks usually explain a positive Hall coefficient with the aid of a sketch which shows carriers moving along the negative second-derivative portion of an energy-momentum curve. This part of the curve corresponds to a relation of the type

$$\mathcal{E} = \mathcal{E}_0 - p^2/2m. \tag{5}$$

This equation also implies that the constant-energy surfaces are concave, and it is this property, not the negative second derivative, which makes R positive.

A generalization of Eq. (5), which more accurately illustrates the factors which determine R, is the following: For a spherical Fermi surface, constant Fermi velocity v_F, isotropic scattering time τ, and degenerate statistics, R will be precisely $+1/ne$ or $-1/ne$ for any shape of $\mathcal{E}$-p curve, according to whether the surface contains electrons or holes. The result is independent of the magnitude of v_F and τ.

Another model which clearly separates the factors which do, and do not, affect R is shown in Fig. 4. This is one example of the planar-faced energy surfaces discussed in the paper mentioned earlier.[87] A simple cubic Brillouin zone is assumed. The occupied volume inside the zone consists of a centered cube and six arms (with square cross sections) extending to the zone faces.

If, as in the previous example, v_F and τ are assumed constant on this surface, R will again be completely determined by the shape of the Fermi surface. The additional feature present in this example is a shape which is a function of the Fermi level. It changes from convex to concave as the band fills. The two parts of Fig. 4 reveal that the unoccupied regions near the top of the band precisely mirror the occupied regions near the bottom of the band.

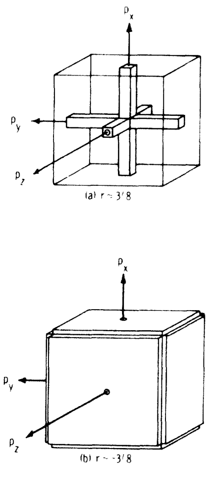

FIG. 4. Polyhedral model to illustrate the evolution of the Hall coefficient R: (a), nearly empty band; (b), nearly filled band.

We might make the assumption that, normal to all faces of the Fermi surface, $\mathcal{E} \propto p^2$. For a crystalline solid, this would be a realistic assumption near the bottom of the band and completely ridiculous near the top. But the value of r is uninfluenced by this lopsided assumption. It is perfectly antisymmetrical, i. e., for equal volumes of occupied and empty momentum space, the values of r are equal in magnitude but opposite in sign.

So far, what we have said in this section is that σ and α respond to the longitudinal properties of electrons, while R is sensitive to their transverse nature. Therefore, these measurements are essentially independent of each other. They can never contradict each other. If the positive α–negative R combination seems peculiar or inconsistent, it is because we have made assumptions, consciously or unconsciously, about the nature of the model.

The assumptions are, of course, that the model has properties similar to those found in conventional bands of crystalline solids. Consequently, certain connections are established among the characteristics of the various transport measurements. But these follow from the nature of the model, not from the measurements themselves.

The viewpoint just developed constitutes the heart of this paper. It leads to the conclusion that n- or p-type behavior cannot be determined from measurements of α or R alone. It shows in fact that the terms "n type" and "p type" are not really adequate to describe the kinds of behavior which can occur when the conventional rules of crystalline behavior do not necessarily apply.

When these rules are not present, it becomes too restrictive to equate p type to the behavior of positive carriers with otherwise normal properties. And such terms as "negative effective mass," "concave Fermi surface," and "missing electron" constitute only partial and possibly unrelated descriptions of electronic behavior.

One way to generalize the language conventionally used to describe electronic properties is to attach the subscripts "ℓ" and "t" (for longitudinal and transverse) to the designations n and p. Then four general types of behavior are possible, as suggested in Fig. 5. This figure is intended to focus attention on the behavior which might be found near the top of the band, but it does not imply that these characteristics are restricted to this region.

The combinations $n_\ell n_t$ and $p_\ell p_t$ identify the conventional kinds of n- and p-type behavior. The designation $n_\ell p_t$ is appropriate for the nearly filled model of Fig. 4(b) (assuming that $\mathcal{E} \propto p^2$). And $p_\ell n_t$ describes the behavior which predominates in range-B liquids.

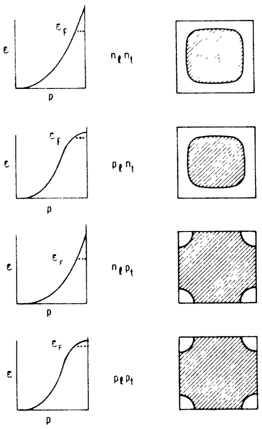

FIG. 5. Generalized definitions of the terms "n type" and "p type" (see Sec. 4), showing four possible kinds of behavior near the top of a band.

5. SIMPLE MODEL FOR RANGES A AND B

We now apply the interpretation developed in Sec. 4 to the experimental transport measurements on liquids. The main goal is to acquire a better understanding of the properties in range B, but we may also use the approach to clarify the questions which we raised earlier about polyvalent metals.

We had pointed out that when polyvalent metals melt, the behavior of σ and R leads to opposite conclusions concerning the effect of melting on the band structure. We can now show that the two descriptions of what happens – a modest change or complete destruction – apply simultaneously. It is just a matter of separating the description into its longitudinal and transverse aspects, as we did for n and p type.

This is illustrated in Fig. 6, which sketches a band model for a hypothetical solid divalent metal in (a) the extended zone representation and (b) the repeated zone representation, and the corresponding situation in (c) the liquid state.

The magnitude of σ is determined by the evolution of the constant-energy surfaces and scattering time τ as a function of energy. The over-all similarity of parts (a) and (c) of Fig. 6 suggests that it is quite possible for the evolution of the surfaces to be affected only slightly by the disappearance of the discontinuities caused by the zone boundaries. Thus the major cause of the change in σ with melting can be ascribed to the change in τ, just as in the monovalent metals. The longitudinal aspect of band structure need only be slightly affected by melting.

But the Hall coefficient is sensitive to the transverse aspects of band structure. The behavior of R in the solid is described most vividly by (b), not (a), since the carriers, as they respond to the magnetic field, do not rotate in sequence around the segments of the large "sphere" in (a), but around the much smaller electron and hole pockets shown in (b). This transverse aspect of the band structure, portrayed in part (b), is entirely destroyed by melting, and is replaced by the large sphere (c), containing all of the valence electrons.

In range B, the predominant behavior is the $p_{\ell} n_t$ variety. It is one of four possible basic types of behavior that were defined in Sec. 4, and there is no need to try to force it to conform to the more specialized solid-crystal kinds of n- or p-type behavior. But in addition, it is possible to argue that the $p_{\ell} n_t$ type of behavior is plausible under the circumstances, without getting involved in details of liquid-state theories.

The Hall coefficients in range B correspond roughly to $n = 2$. Hence the de Broglie wavelengths of the most energetic electrons are approaching the magnitude of the average nearest-neighbor distance. This is all that is necessary to bring on the p_{ℓ} type of behavior in σ and α. The properties of the many one-dimensional periodic-potential models which have been investigated testify to that.

But the p_t kind of behavior follows only from a concave Fermi surface, and that requires the presence of a well-defined oriented three-dimensional set of Brillouin-zone faces. This, we believe, demands a more extended and special kind of atomic arrangement in the liquid than that which leads to a well-defined peak in the radial distribution function. Once again, it is necessary to distinguish between the longitudinal and transverse aspects of the atomic arrangements in the liquid. These observations lead us to conclude that a positive R is the solid-state property least likely to be observed in liquids. The environment may be anisotropic, but not in the systematic and extreme sense that would cause most of the electrons to be deflected to the wrong side in the presence of crossed electric and magnetic fields.

How many of the predominant experimental characteristics could be accounted for by a simple model which incorporates the $p_{\ell} n_t$ type of behavior? The characteristics of the measurements in ranges A and B and their smooth evolution as a

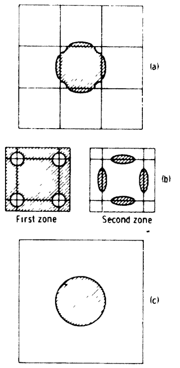

FIG. 6. Fermi surface for a hypothetical divalent metal: (a) and (b), the solid state, in the extended and repeated zone representations, respectively; (c), the liquid state.

function of σ suggest that we should seek a single-band basically metallic model to describe the data. The model should be capable of a continuous "deformation" such that the normal $n_\ell n_t$ properties of range A will gradually transform into the $p_\ell n_t$ characteristics which dominate in range B.

A very simple model which can qualitatively account for this behavior is the one which Mott first applied to liquid Hg,[90] and which was later extended to a discussion of liquid "semiconductors".[2] The essential feature of this model, as Mott described it, was a dip in the density-of-states-versus-energy curve, but for the present purposes it is more convenient to discuss its properties in terms of the σ-versus-$\mathcal{E}$ curves shown in Fig. 7.

We postulate that the model is such that the dependence of σ on the Fermi level $\mathcal{E}_F$ is the same as the hypothetical kind of variation of σ with $\mathcal{E}$ that is implied in Eq. (4). The shading which is attached to curve 3 in Fig. 7 implies that the electronic states are localized in that range. This will be discussed later. For the present, however, we will apply the model in its simplest, purely metallic form, i.e., all energy states above the zero of conductivity are the conventional nonlocalized variety.

In three dimensions, the Fermi surface of the model is simply a sphere, or at least an essentially convex surface. The carrier density which it encloses is to be regarded as a parameter which may be adjusted at will to fit the experimental data.

The sequence of curves 1, 2, 3 in Fig. 7 shows how the model changes as σ is reduced. The minimum in the density of states which develops (which Mott called a "pseudogap") corresponds to the region of energy overlap between the first and second bands in the case of a divalent metal. In the case of a liquid which was a semiconductor in the solid state, it corresponds to the remnant of the filled-in gap which had existed in the solid phase.

As σ decreases, the slope of the $\sigma(\mathcal{E}_F)$ curve changes from positive to negative and grows more steeply negative. According to Eq. (4), α changes from negative to positive and then increases in magnitude. But the large, positive α does not correspond to a small, semiconductorlike density of holes. In keeping with the approach of Sec. 4, there is no link between the signs or magnitudes of α and R, and hence there is no contradiction between the large, positive α and the small, negative R.

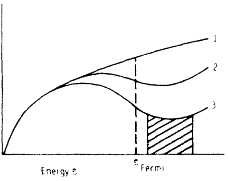

FIG. 7. Simple model to describe the predominant properties in ranges A and B of Table I.

In the case of binary liquids which form ordered solids, the depth of the minimum in the density of states is a measure of the extent to which atoms X are adjacent to atoms Y, and vice versa. As the temperature rises, it is natural to expect that the "strength" of this local X-Y ordering will decrease. Then the minimum in the density of states will become more shallow, and σ will rise.

Thus the curves in Fig. 7, in the reverse order 3, 2, 1, can be used to describe the effect of raising T. With increasing temperature, the positive α should decrease in magnitude. According to Fig. 7, raising T inevitably brings the liquid into the more conventional metallic state. Therefore at high enough temperatures, σ should stop increasing and start to decrease again, as has been observed in at least six cases thus far.

We have postulated a metallic model, so that the positive $d\sigma/dT$ indicates, according to Eq. (1), that the mean free path is increasing with increasing T. We also noted that the X-Y ordering decreases as T rises. Both trends predict that the effect of anisotropy on the magnitude of R will weaken as the temperature is increased.

If anisotropy has affected the Hall coefficient near the melting point, then R should increase with increasing T until it reaches the isotropic value for the given carrier density.

The above predictions are in accord with all of the predominant experimental characteristics identified in ranges A and B of Table II.

Finally, the simple model of Fig. 7 may be applied to the composition dependence of the transport behavior. The notion that local X-Y ordering lowers σ also seems applicable here, since the cusplike minima were seen at stoichiometric compositions where the ordering can develop to the maximum extent. The complete or nearly complete disappearance of the σ minimum which is observed at higher temperatures in several cases is then simply a consequence of the disappearance of the ordering.

The behavior of nonstoichiometric compositions is now much easier to explain since we have postulated that the stoichiometric X-Y composition, the pure metallic component X, and the pure nonmetallic component Y are all variations of the same basically metallic model. The properties at intermediate compositions may be interpreted as a weighted average of the properties of the stoichiometric X-Y liquid and pure Y, or of X-Y and X.

The general nature of the behavior in these two intervals is determined by the values of σ at the ends of the intervals. Thus, for example, there is no basic change in the transport characteristics between SnTe and Te, since both liquids share the same set of properties which predominate in range

B. In particular, there is no reason to anticipate a disappearance of the semiconductorlike characteristics or the appearance of a σ maximum at intermediate compositions.

On the other side of stoichiometry, the properties evolve more rapidly because the conductivity of X is much higher than that of the stoichiometric liquid, and because the characteristics of the intermediate compositions must undergo a basic change, since component X is a conventionally metallic liquid from range A.

We might note that $d\sigma/dT$ changes sign at about 6000 and 3000 Ω^{-1} cm^{-1} on the metal-rich sides of Ag_2Te and SnTe, respectively.[29] It is difficult to determine the precise σ level at which this occurs from the published data, but at least these values are in rough accord with the σ level which separates ranges A and B.

We also wish to note that there is no reason to associate a change in composition with the rise or fall of a Fermi level, linking it to some parameter such as the average valence. The lack of such a need is clearest in the case of Te-rich liquid tellurides, since the Hall data suggest that both the stoichiometric liquid and pure Te contribute approximately two conducting carriers per atom. On the other hand, we cannot put forth a simple model to trace out the composition dependence of the carrier density in the corresponding selenides, since R for Se is so much larger than R_0.

To explain the predominant characteristics of the experimental data in range B, it was necessary to place the Fermi level on the negative-slope portions of curves 2 and 3 in Fig. 7. We did not need to specify whether or not these curves stop decreasing and begin to rise again, and we assumed that all electronic states were nonlocalized.

If the density of states in the pseudogap of the Mott model drops to a low enough value, however, the states near the bottom will become localized.[2, 3, 75] This is suggested by the shading attached to curve 3 in Fig. 7. How would this additional feature affect the properties of the model?

We might argue that the model has edged closer to a true p-type semiconductor model, since a specific number of empty nonlocalized states is now defined. When the temperature is raised, carriers will be excited from the nonlocalized to the localized states, thus decreasing $\mathcal{E}_F$, increasing σ, and decreasing α. So we find the same qualitative behavior as before, except that the temperature dependence is now linked to an increase in p rather than to the changing character of the $\sigma(\mathcal{E})$ curves.

From a semiconductor point of view, the density of localized states in the pseudogap can become very large. One estimate is 10^{20} cm^{-3}.[91] But the Fermi surface remains convex and still encloses a much larger carrier density of the order of 10^{22} cm^{-3}. Even if the temperature were raised enough to fill all of the localized states, there would only be a slight, probably undetectable increase in R. Hence, it is possible for the Hall coefficient to retain its n-type temperature-independent nature, although the carrier transfer may at the same time have a major effect on σ and α.

This modified model provides a further illustration of the inadequacies of the language of crystalline physics. Introducing the localized levels has defined a band (i.e., a bounded interval) of normally conducting states. Placing $\mathcal{E}_F$ near the top of this band can lead to a small temperature-dependent hole density, and hence we could argue that this qualifies as a p-type semiconductor model.

The difficulty is that we have created a band only in a one-dimensional sense. If we look in three dimensions, we do not find anything resembling the normal characteristics of a band maximum, because there are no true Brillouin-zone boundaries present. We see nothing but large convex Fermi surfaces near the band maximum, while at slightly higher energies, the Fermi surface is no longer defined.

We might go one step further and postulate the existence of an additional band of nonlocalized states beyond the pseudogap. Now we have a two-band model, but again only in a partial sense. The gap between the bands is not a zone boundary but simply a spherical surface of energy discontinuity. Constant energy surfaces near the top of the first band and near the bottom of the second could both be convex and practically indistinguishable from each other. Excitation of significant numbers of carriers across the pseudogap need have little effect on R, although σ and α could exhibit conventional semiconducting characteristics.

Optical measurements indicate that some noncrystalline systems do retain forbidden energy gaps.[92] We will not take issue with such an interpretation, but the present paper is confined to transport measurements, and we do not feel that excitation of carriers across an energy gap is required to explain any of the characteristics which predominate in ranges A and B.

6. TRANSPORT BEHAVIOR IN RANGE C

No sudden jump in the magnitude of σ occurs in going from range B to C. Qualitative calculations suggest that this is reasonable.[2] There is no qualitative change in the behavior of σ and α, so that the nonlocalized model of Sec. 5 could be used to describe the properties of these two coefficients in range C also.

But this ignores the fact that the nature of the conductivity has undergone a fundamental change in range C. Furthermore, the model cannot account for the large temperature-dependent values of R which have been found in range C.

The characteristics most commonly observed in range C have been an activation-energy kind of behavior in R and σ, such that the Hall mobility is practically temperature-independent.

The presence of activation energies should not tempt anyone to describe the liquids as semiconductors. We feel that the language of crystalline solids loses all relevance in range C. It seems about as reasonable to use band-structure terms here as it would to apply them to a set of isolated atoms.

The hopping model in range-C liquids should not be equated with the hopping regime of impurity-band conduction in semiconductors. In the latter case, the electrons, although associated with disordered impurities, are imbedded in a crystalline medium which profoundly influences their properties.[93, 94] For example, positive Hall coefficients have been seen in impurity-band semiconductors.[93]

In range-C liquids, the Hall coefficients thus far reported have all been negative. In a certain sense, a localized electron possesses a greater degree of classical reality than a nonlocalized band electron. It is difficult to imagine how the disordered environment could cause these real, localized charges to be deflected to the wrong side by the crossed electric and magnetic fields as they hop from one site to another.

7. CONCLUDING REMARKS

In this paper, we have developed an approach to the interpretation of transport measurements which we believe is useful under more general circumstances than those encountered in crystalline solids. We used this approach to discuss the behavior of electronically conducting liquids, and we feel that it does help to resolve a number of the difficulties that have made the transport properties of some liquids seem complicated and contradictory.

The approach may well have application to other kinds of disordered systems such as glasses and amorphous films. We have not attempted to survey the literature in these other areas with any degree of thoroughness, but we are aware of some discussions which also seem to suffer from an overly restrictive, crystalline solid-state kind of approach.

We tried to make it abundantly clear that the thermoelectric power and the Hall coefficient measure different aspects of electronic behavior. Consequently, they can never contradict each other, nor can each measurement alone provide adequate information about the electronic properties. In retrospect, it seems unfortunate that the description of liquids from ranges B and C which developed over the years was based almost entirely on measurements of the thermoelectric power and electrical conductivity.

We have also implied that a better understanding of liquids and other noncrystalline systems can be achieved by discussing separately the longitudinal and transverse aspects and consequences of atomic arrangement and band structure.

The variety and complexity of transport data on liquids will undoubtedly increase as more and more results appear. Consequently, this seemed to be an appropriate time to point out the remarkable uniformity of the measurements which have accumulated thus far, and to demonstrate that most of these measurements, when properly interpreted, can be described in terms of a simple and plausible model.

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Interferometric Study of Dissociative Recombination Radiation in Neon and Argon Afterglows*

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A photoelectric recording, pressure-tuned Fabry-Perot interferometer of high resolution is used to determine the spectral line profiles of 22 neon and 5 argon ($2p_n \rightarrow 1s_m$) lines emitted from a microwave discharge and during the ensuing afterglow. All afterglow line profiles are broader than the corresponding discharge lines, and in most cases the afterglow line shapes are consistent with a dissociative origin of the excited atoms, indicating that the $2p_n$ excited states of neon and argon are produced by dissociative recombination of electrons with Ne_2^+ and Ar_2^+ ions, respectively. Detailed examination of the line profiles in neon indicates a "multishouldered" structure corresponding to several different dissociation kinetic energies, suggesting that different initial states of the Ne_2^+ ion are involved in the dissociative recombination process. From the deduced molecular ion energy levels it appears that, in addition to the Ne_2^+ ion state with a dissociation energy $D = 1.35$ eV reported by Connor and Biondi, there may be a more weakly bound state with $D \sim 0.5$ eV which contributes to the recombination.

I. INTRODUCTION

In an earlier study,[1] the capture rate of electrons by ions in neon was shown to result from the dissociative recombination process, i.e.,

$$\mathrm{Ne}_2^+ + e \rightleftharpoons (\mathrm{Ne}_2^*)_{\text{unstable}} \rightleftharpoons \mathrm{Ne}^* + \mathrm{Ne} + \text{kinetic energy}\ , \qquad (1)$$