LIQUID SEMICONDUCTORS

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PREFACE

The definition of liquid semiconductors as a research area seems to date back to a review article by Ioffe and Regel (1960). Information and understanding about liquid semiconductors has since advanced to the point where various investigators are beginning to propose or consider some general models for liquid semiconductor behavior. A review of this subject thus seems worthwhile in order to consolidate critically the existing information and to provide a stronger basis for further progress.

The main goal of this work is to present a discussion of the present status of the field of liquid semiconductors that will be of value for present and future workers in this and related areas. The book also provides an opportunity to set forth my own views about promising approaches for understanding liquid semiconductor behavior and, I hope, to stimulate much-needed investigations of these materials by scientists who have expertise in a number of methods not yet extensively applied to liquid semiconductors, such as NMR or diffraction techniques. There are many fertile opportunities for valuable and interesting work that have been obscured by the lack of a comprehensive source of information, and perhaps this monograph may correct the situation. The properties and nature of liquid semiconductors suggest many concepts and problems that are of value and interest to scholars interested in the physics or chemistry of condensed matter, and in this volume these concepts and problems are made available to readers with only general interest in or curiosity about the subject.

In keeping with these purposes, the material is presented at a level accessible to a reader moderately knowledgeable in solid state physics. This requires a compromise between testing the patience of better-informed readers and asking others to refer back to more basic sources. No effort is made to be encyclopedic in references to experimental and theoretical work on the subject, as might suit a reader with some detailed interest in one specific topic. The references should be sufficient to provide good starting points for an investigation of the literature. Inevitably, the extent of discussion will be colored by my own background and interests in a way that will be obvious to a perceptive reader.

The central area of interest is the electronic behavior of liquid semiconductors. This behavior is the most striking and unique property of these materials and a key to understanding them. This is not to belittle structural, thermochemical, and other aspects of the subject, for which unfortunately there is a great deficiency of information. Thus, it is not possible to include as much material about nonelectrical aspects. At this point, it is appropriate to refer to the monograph by Glazov, Chizhevskaya, and Glagoleva (1969), "Liquid Semiconductors," which treats the subject from a physicochemical point of view. In the present book, chemical and metallurgical aspects are discussed in a way that provides a rounded presentation, but the emphasis is on electronic aspects.

Liquid and amorphous semiconductors may be regarded as different facets of a broader domain of study, that of disordered electronically conducting systems. This common domain has become an increasingly active field of research, and the rate of progress in it has recently accelerated. A major part of this new activity is concerned with solids, but the theoretical developments have broad application, and there are other overlapping areas. The reader is referred to recent monographs on the broader subject of disordered systems: "Electronic Processes in Non-Crystalline Materials," by Mott and Davis (1971), and "Amorphous and Liquid Semiconductors," edited by J. Tauc (1974). An earlier treatise that has contributed to the subject is A. I. Gubanov (1965), "Quantum Electron Theory of Amorphous Conductors." Another important source of information is to be found in proceedings of international conferences, which have been held every two years on amorphous and liquid semiconductors, the most recent one (the sixth) at Leningrad in 1975.

The organization of this monograph is determined by the state of development of the field and my own approach (as an experimentalist) toward understanding the subject. The field is in a rather early stage of development, in which the appropriate concepts for proper understanding are only beginning to be apparent. Consequently the most concrete facts are the experimental data and the questions they raise. Accordingly, the chapters fall into three main sections following the introduction, which serves to define the field of investigation and consider its relationship to other classes of materials. The first section (Chapters 2–4) is a systematic review of experimental information, with the purpose of uncovering some of the basic questions posed. Chapters 2 and 3 concentrate, respectively, on physical and on chemical or metallurgical information. It also seems desirable to include a chapter (Chapter 4) that reviews experimental methods and problems having particular significance for the study of liquid semiconductors. The second section (Chapters 5 and 6) discusses the theoretical basis for interpreting the experimental behavior. Chapter 5 considers the theoretical and conceptual basis for understanding or describing the electronic structure, and Chapter 6 the theory for interpreting the various experimental measurements. In this section, we emphasize those results that seem to be fairly well established, and we defer discussion of more tentative or speculative theories. The final section (Chapters 7 and 8) aims at examining existing information about various liquid semiconductors in the light of existing theories and concepts in order to determine what specific conclusions can be derived. The extent to which this can be done depends strongly on the amount and diversity of reliable data available for each liquid semiconductor system, as well as how the results have lent themselves to coherent explanation. Thallium–tellurium alloys are well favored by both these criteria, and Chapter 7 is devoted to this system and pure tellurium. Many other alloy systems have elements of behavior that can be profitably compared with or contrasted to that of Tl–Te. Discussions of other alloy systems are conveniently grouped together in Chapter 8.

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It is appropriate to acknowledge and express my appreciation for the stimulus to this work provided by interactions with others in this field. The provocative data obtained by former associates and students in my laboratory—Charles E. Mallon, James F. Leavy, Marshall B. Field, James M. Donally, Michael M. Dahl, and Robert L. Petersen—have provided reliable and fertile material for use in trying to formulate explanations for liquid semiconductor behavior. The development of my understanding of the subject has benefited from discussions—sometimes lively ones—with many other investigators in the field. I am indebted to J. C. Perron and D. N. Lee for making available to me unpublished work from their doctoral theses. I am grateful to William W. Warren, Jr., Jan Tauc, and John A. Gardner for critical comments on parts of the manuscript. This work owes its greatest debt to Professor Sir Nevill Mott. Besides his many important direct contributions to the subject, which will be evident in what follows, this work has benefited from my many interactions with him, including a sabbatical year in his laboratory, which have encouraged and stimulated my study of the subject and illuminated my understanding.

CONTENTS

CHAPTER 1

INTRODUCTION

Semiconducting liquids are a poorly understood class of materials as compared to others, such as liquid metals or molten salts, where first-approximation models exist (for example, the free electron gas model for metals, or the Born model for ionic materials). There is no simple model which is generally accepted as a first approach for explaining the behavior of liquid semiconductors, and the development of the appropriate concepts for doing this poses a challenging problem.

The physical character of liquid semiconductors puts them in an intermediate position between several other classes of materials: liquid metals, molten salts, molecular liquids, and amorphous solids. It is often difficult to define the boundaries precisely. Some clarification of the interrelations will be one of our goals, and it will be pursued to some extent in this introductory chapter. Through these relationships, present understanding of other materials can be used in solving problems concerning liquid semiconductors. Conversely, an improved understanding of liquid semiconductors can be expected to add a deeper insight into the character of the better known substances.

To place the discussion on a more solid footing, it seems best to start by defining liquid semiconductors. The definition used by Ioffe and Regel in their pioneering review article (Ioffe and Regel, 1960) serves as a rough starting point: Liquid semiconductors are electronically conducting liquids with electrical conductivities less than the usual range for liquid metals. This distinction from molten salts and molecular liquids, which do not conduct electronically, seems simple, but it will require some elaboration. At the other end of the conductivity range, the line of distinction from liquid metals is arbitrary and has been a subject of some controversy. Ioffe and Regel have suggested that liquids with electronic conductivities less than $\sim 10^4$ ohm^{-1} cm^{-1} (the value for liquid mercury) should be regarded as liquid semiconductors. We discuss this in more detail below.

Before discussing further the boundaries of liquid semiconductors with other classes of liquids, let us outline briefly what kinds of materials are commonly regarded as liquid semiconductors. Among the elements, molten selenium and molten tellurium fall into this category. Other elements which are semiconductors in the crystalline state, such as Ge and Si, become metals on fusion. The same is true for many compound semiconductors such as the III–V compounds. This change from a semiconductor to a metal on melting has been correlated by Ioffe and Regel (1960) with a decrease in the atomic volume. Thus the well-known association of crystalline semiconducting behavior with a large atomic volume and a small coordination number seems to be preserved in the liquid state. Many other compounds, such as In_2Te_3, increase in volume on melting or else have relatively small decreases in volume, but nonetheless have electrical properties associated with semiconducting liquids. This relationship is discussed in more detail in Section 3.2.

Early studies of liquid semiconductors were based mainly on observing what happens to the electrical behavior when crystalline semiconductors are melted, but since liquids can have wide ranges of stoichiometry, liquid semiconductors are better regarded as alloy systems in which the composition is a continuous variable. In this frame of reference, liquid semiconductor systems include Se–Te, Tl–Te, Tl–Se, Ag–Te, Mg–Bi, V–O, and many other binary systems. Obviously, very many tertiary or more complicated systems would fall in this category over some ranges of composition, but at the present stage of development, the added complexity of more than one composition variable does not often help to shed light on the basic questions. Consequently, there have not been very many studies of tertiary systems. Tertiary systems which have been studied profitably include ones which can be regarded as pseudobinary systems such as Ga_2Te_3–Ga_2Se_3, and systems in which a third element is added as a "doping" agent in a binary system of fixed composition such as Tl–Te–M and Tl–Se–M, where M represents a relatively small amount of an element such as Cd, In, or Sb. The reader may have noted the frequent occurrence of a chalcogenide element in systems which have been mentioned. Most known liquid semiconductor systems do contain a group VIB element. Although this correlation is not universal, it is a significant characteristic of liquid semiconductors which needs to be understood.

The definition of the boundary between liquid semiconductors and insulating liquids such as molten salts and molecular liquids, although simple at first sight, shows some complexity on deeper examination. It is clear that electronic conduction and ionic conduction can occur in parallel in molten salts, and one or the other may dominate in some systems depending on the temperature or other conditions. As noted by Ioffe and Regel (Ioffe and

Regel, 1960), the electrical conductivity σ of an ionic liquid is unlikely to be larger than ~ 1 ohm^{-1} cm^{-1} because of the limited ionic mobility, so that liquids with higher conductivities must conduct electronically. When σ is lower than that, other considerations, such as measured ionic transport numbers or the chemical nature, must be used to establish the extent of electronic conductivity.

A substance such as liquid selenium has a strongly temperature-dependent electrical conductivity which may be as low as 10^{-7} ohm^{-1} cm^{-1} near the freezing point. Its chemical nature indicates that it is a covalent rather than an ionic substance. A possible mechanism for electronic transport in such a material is by hopping of electrons in localized states which may be charged. If so, the charged molecular complex can drift in an electric field, thus giving it the character of an ionic liquid, albeit a dilute one. Furthermore, recently developed concepts about the nature of electronic motion in localized states suggest the possibility of a wide range of correlation between the motion of the charge and the motion of the associated molecular complex. In view of this, the distinction between ionic transport and hopping transport of electrons in localized states may not be sharp in liquids. This is one of the subjects which needs to be clarified in future studies.

There are some types of electronically conducting liquids other than liquid metals which are not conventionally regarded as liquid semiconductors. One of them consists of solutions of alkali metals or alkaline-earth metals in ammonia or related liquids (Cohen and Thompson, 1968). These are low temperature molecular liquids in which electrons can occur in localized or extended states, depending on the concentration of the metal ions. A second type includes a number of molten halide salts which dissolve large amounts of the metal, such as La–$LaCl_3$, Bi–BiI_3, and molten alkali halides with excess metal (Bredig, 1964). The distinction between metal solutions in molten salts and liquid semiconductors is mainly conventional. All graduations can be found in the ionicity between these substances and systems conventionally regarded as liquid semiconductors, so that only quantitative distinctions can be made. It will be seen later that a "dilute metal" model provides a useful way to explain the behavior of many liquid semiconductor systems in certain ranges of composition, and this is not qualitatively different from reasonable models for these two types of systems. Therefore there is probably considerable overlap.

The boundary with liquid metals has been the subject of some controversy, and it represents a topic to be clarified through study of the nature of the intermediary materials rather than be debated. Semiconducting liquids in the high conductivity range ($\gtrsim 100$ ohm^{-1} cm^{-1}) are statistically degenerate and obey Fermi–Dirac statistics. In this sense, they are metals, and the name liquid semiconductor is partly a historic accident. Probably one reason they were called semiconductors is that in many cases they show a strong increase in conductivity with temperature, in contrast to typical liquid metals, and like solid semiconductors in the classical (now obsolete) definition. Recent studies (Cutler, 1971a) indicate that in some cases this sensitivity to temperature cannot be ascribed to excitation of carriers across a gap or out of traps, but must reflect a change in chemical structure with temperature. Therefore the mechanism for the temperature sensitivity of the electrical conductivity may be different from conventional semiconductors. Ioffe and Regel (1960) emphasized the fact that the mean-free path in semiconducting liquids is of the order of the interatomic distance, in contrast to liquid metals. It has become established that the Ziman theory for electronic transport, based on weak scattering, provides a good description of transport in liquids with electrical conductivity $\sigma \gtrsim 10^4$ ohm^{-1} cm^{-1}. On the other hand, other approaches to transport theory, based on strong scattering, seem to be applicable for $\sigma \lesssim 2500$ ohm^{-1} cm^{-1}. (This subject is discussed more thoroughly in Section 6.1.) Therefore liquids with $\sigma \lesssim 10^4$ ohm^{-1} cm^{-1} apparently differ in some important respects from the usual liquid metals, and as the conductivity is decreased, some of the classical concepts of semiconducting behavior seem to become increasingly pertinent. Certainly, in the range where $10{,}000 \gtrsim \sigma \gtrsim 1000$ ohm^{-1} cm^{-1}, investigators whose main concern is liquid metals or liquid semiconductors may feel equally at home.

The nature of the boundaries between liquid semiconductors and ionic, molecular, or metallic liquids has many similarities to solids. However, the pecularities of the liquid state lead to important differences. As noted already, diffusive motion of atoms in the liquid may play a special role in electronic transport when electrons are in localized states. Another difference, which arises from the wide range of stoichiometry which can occur in the liquid state, is that the electronic structure changes continuously in response to changes in chemical composition. We believe this to be the most important attribute of liquid semiconductor behavior. This characteristic offers an opportunity for developing a deeper understanding of one of the basic problems in the physics and chemistry of condensed matter, that is, the mutual relation between the electronic structure and the atomic or chemical structure of matter. It seems likely that the chemical structure of many liquid semiconductor systems is based on covalent bonding, but in contrast to the common molecular liquids, the high temperature and chemical environment is one in which the resulting molecular species are not well-defined (especially at present). Thus a rapidly changing dynamic equilibrium between various atomic arrangements probably plays a role in determining the effect of changes in temperature or composition. In addition to this, the binding which occurs in liquid semiconductor systems can range continuously to the extremes of ionic or metallic binding. Thus we are concerned with a type of matter which is an unusual "soup" from a conceptual as well as physical point of view, for which many of the usual concepts or models are not adequate. The resulting problems seem to call for attention by theoretical chemists as well as physicists, and the resolution seems likely to provide valuable insights for both fields.

Liquid semiconductors also have a special relationship to solid amorphous semiconductors. The fact that there is a liquid rather than a solid has no significance in many aspects of electronic behavior, since the time scale for many types of electronic motion is much faster than for atomic motion, and the same concepts or theories are applicable. The aspects of behavior in which the fluidity is significant are mainly those already mentioned, and they are not the dominant element in electrical behavior. However, there are many practical or quantitative differences which cause a considerable difference in emphasis. For one thing, most of the systems are liquid in the high temperature range of 400–1000°C, and no semiconducting melts are known below 170°C. Thus, low temperature types of studies are out of the picture. This, together with certain chemical factors to be discussed later, leads to the result that liquid semiconductors typically have much higher concentrations of electronic carriers than amorphous solids. As indicated earlier, many liquid semiconductors are nearly (or completely, depending on your point of view) metallic, whereas most typical amorphous semiconductors are more closely related to insulators. In terms of the electronic structure, this means that amorphous solids very frequently represent situations where the Fermi energy is well separated (in units of kT) from energies where extended states occur (conducting bands), while liquid semiconductors typically have the Fermi energy near or within conducting bands. This is not by any means a universal dichotomy; liquid selenium is a very respectable insulator, and one could also lay claim to liquid sulfur, an excellent insulator, as a liquid semiconductor. Conversely, many amorphous solids have been made with metallic or near-metallic properties.

From a practical point of view, some other distinctions between amorphous solids and liquid semiconductors should be mentioned. Assured achievement of homogeneity is usually a relatively simple experimental problem for liquids, whereas preparation of reproducible amorphous solid samples is difficult except possibly for natural glasses, which occur only in restricted ranges of compositions. On the other hand, as already noted, the fact that liquids must be studied at high temperatures presents special experimental problems and places important limitations on what can be done experimentally.

CHAPTER 2

EXPERIMENTAL INFORMATION ON PHYSICAL PROPERTIES

In this chapter and Chapter 3, we review existing experimental information about liquid semiconductors. The present chapter is concerned with physical properties, and the following one with chemical and physiochemical properties. Our purpose is to set forth what is generally known experimentally about these substances, and the information presented will often be representative rather than exhaustive. In later chapters, we consider the applicability of present theoretical knowledge to existing experimental information.

Of all the physical properties, the electronic transport parameters are the most distinctive ones for liquid semiconductors. Therefore, it is not surprising that a large fraction of existing information consists of studies of the electrical conductivity σ, which is the most easily measured transport parameter. Measurements of the thermopower S (Seebeck coefficient), Hall coefficient R_H, and thermal conductivity κ are carried out with rapidly decreasing frequency. We devote a section to each of these measurements as well as one on the magnetic susceptibility χ_M. Studies of nuclear magnetic resonance and optical properties are so sparse that it will be more appropriate to combine the presentation of existing information with discussion of their interpretation. This will be done in Chapters 6–8.

2.1 ELECTRICAL CONDUCTIVITY

Many of the early studies of liquid semiconductors consisted simply of measurements of the electrical conductivity σ of molten versions of solid semiconductors (Ioffe and Regel, 1960). The initial concern was to determine which solids remain semiconductors in the liquid state. The reported information is frequently limited to a curve for σ as a function of temperature T, taken through the melting point. Figure 2.1 shows some typical curves of this sort. As mentioned earlier, many solid semiconductors, such as