POLARONS

Emin provides experimental and theoretical graduate students and researchers with a distinctive introduction to the principles governing polaron science. The fundamental physics is emphasized and mathematical formalism is avoided. The book gives a clear guide to how different types of polaron form and the measurements used to identify them. Analyses of four diverse physical problems illustrate polaron effects producing dramatic physical phenomena.

The first part of the book describes the principles governing polaron and bipolaron formation in different classes of materials. The second part emphasizes the distinguishing electronic-transport and optical phenomena through which polarons manifest themselves. The book concludes by extending polaron concepts to address critical aspects of four multifaceted electronic and atomic problems: Large-bipolaron superconductivity, electronic switching of small-polaron semiconductors, electronically stimulated atomic desorption, and diffusion of light interstitial atoms.

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Preface

In 1927 Born and Oppenheimer formalized the notion that electrons in condensed matter generally follow the relatively slow motions of atoms which themselves adjust to the electrons' averaged locations. In 1933 Landau advanced this idea in suggesting that an electron added to an insulator such as sodium chloride could become *self-trapped*. The electron is then bound in the potential well produced by displacing the equilibrium positions of surrounding atoms from their carrier-free values to those stabilized by the carrier's very presence. Self-trapped carriers move very slowly since they only move when the associated atoms move.

The term *polaron* often refers to the unit comprising a self-trapped carrier and the associated pattern of displaced atomic equilibrium positions. However, the term polaron is also used in a more general sense to designate an electronic carrier and the altered atomic motions induced by it. Then polarons whose electronic carriers are not self-trapped are labeled as *weak-coupling polarons*. By contrast, polarons whose electronic carriers are self-trapped are termed *strong-coupling polarons*.

In some instances polaron motion can be regarded as quasi-free albeit with occasional interruptions by scattering events. The effective mass of a weak-coupling polaron is only slightly larger than that of its bare electronic carrier. By contrast, a strong-coupling polaron's effective mass is very much larger than that of the bare electronic carrier.

These scattering treatments of polaron motion presume its coherence. The motion's transfer energy must then exceed the energy variations and uncertainties which accompany the polaron's movement and scattering. For instance, a strong-coupling polaron's motion is coherent if the electronic transfer energy between adjacent sites exceeds changes of its self-trapped carrier's energy which occur as atoms move classically to enable this transfer. This condition is satisfied when the electronic transfer energy is large enough for the self-trapped carrier to extend over at least several sites. Thus a *large*-polaron's motion is coherent.

By contrast, a *small* polaron has its self-trapped carrier primarily confined to a single site. A stable small polaron only forms when its self-trapped carrier's electronic transfer energy is sufficiently small. For such small values of the electronic transfer energy the self-trapped carrier's response to classical atomic motion is incoherent. Small-polaron transport then proceeds by a succession of thermally assisted jumps.

In an unperturbed ideal crystal small-polaron motion becomes coherent at low temperatures when atoms' motions become non-classical. Then the inter-site motion of a self-trapped carrier occurs as the atoms of the small-polaron's atomic displacement pattern collectively tunnel between geometrically equivalent displaced equilibrium positions. However, the small-polaron transfer energy associated with such motion is extremely small, much smaller than the characteristic phonon energy. Small-polaron transfer energies are usually small enough to be dwarfed by the site-to-site energy differences of a real material. As a result small-polaron motion in actual materials is generally regarded as incoherent even at very low temperatures.

This physical picture was already established half a century ago when I began my studies of the formation and properties of polarons. Nonetheless, important issues remained unresolved. It was necessary to proceed beyond oversimplified models to understand how polarons and self-trapped paired carriers' bipolarons form. Hopping transport needed to be treated beyond the unrealistic non-adiabatic limit, generally restricted to electronic transfer energies that are much smaller than even phonon energies. Means were needed to distinguish between intrinsic small-polaron hopping and extrinsic multi-phonon-assisted hopping involving defects and dopants. Many effects of the shifts of atoms' vibration frequencies arising from self-trapped carriers' polarizabilities required consideration. These topics are addressed within this book's discussion of polarons.

The book's seventeen chapters are divided into three sections. In the first section I explain how and when different types of polaron form. In the second section I address polarons' distinctive electrical transport and optical properties. It is through these properties that polarons can be identified. The final section considers four dissimilar electronic and atomic phenomena for which polaronic effects may be critical.

Throughout this discussion I stress the underlying physics governing polaron formation and motion. I eschew formal mathematics and oversimplified models. I make no attempt to review the rich formalisms that have been developed to address the many-body problem of interacting electrons and phonons. As such, this book does not mirror the totality of present polaron research.

This exposition on polaron physics is an idiosyncratic account. I emphasize several important consequences of carrier-induced softening, a frequently neglected

phenomenon. I also address some topics such as small-polarons' hopping conduction and the Hall effect in exceptional detail in order to highlight overlooked features of these phenomena. Furthermore, I even advance the unorthodox view that some heavily doped materials' electronic hopping conduction occurs between defect-related sites rather than between intrinsic sites. I also argue that a phonon-mediated attraction between large bipolarons can drive their condensation into a liquid. This large-bipolaron liquid, analogous to liquid ^{4}He, could be a precursor to further condensation into a superconducting state. I present a heterodox explanation of the driving mechanism of electronic switching in low-mobility solids. Finally, the concepts of small-polaron formation and motion are extended to address electronically stimulated atomic desorption and light-atom diffusion.

To put this treatise's distinctive ideas in context I now succinctly describe them within a summary of the polaron physics' intellectual framework. These concepts involve (1) polaron and bipolaron formation, (2) polaron and bipolaron properties and (3) several problems to which extensions of core polaron notions have been applied.

Polaron formation concerns an electronic carrier interacting with relatively slow-moving atoms in accord with the adiabatic principle. Atoms accommodate to a suitable average of the carrier's position while the carrier adjusts to atoms' instantaneous positions. *Carrier-induced softening* describes the energy lowering resulting from carriers adjusting to atoms' vibrations. The binding energy of a weak-coupling polaron arises solely from the dynamics of this electronic response. As such, the energy lowering associated with forming a weak-coupling polaron vanishes in the adiabatic limit. In this limit atoms' vibration frequencies approach zero as atomic masses become infinite while vibrations' stiffness constants remain finite. By contrast, a strong-coupling polaron involves atoms vibrating about the equilibrium positions they assume to form the potential well within which the self-trapped carrier is bound. Thus, a strong-coupling polaron's energy lowering does not vanish in the adiabatic limit where atoms' vibrations are suppressed.

The size of a self-trapped state generally depends on its carrier's electron–phonon interactions. A carrier has long-range electrostatic interactions with the displaceable ions of a polar medium. A carrier also has short-range interactions with the displaceable atoms that it contacts. These electron–phonon interactions drive carrier-induced shifts of atoms' equilibrium positions and vibration frequencies. Both effects alter the coupled system's free energy. Nonetheless, the size of a carrier's self-trapped state is usually determined by minimizing the energy of its strong-coupling polaron in its adiabatic limit where atoms' vibrations are ignored.

With just the three-dimensional long-range electron–phonon interaction the spatial extent of a self-trapped state is a continuous function of the physical parameters. Then the self-trapped carrier's radius is $R_p \equiv (\hbar^2/m^*e^2)[\varepsilon_\infty/(1-\varepsilon_\infty/\varepsilon_0)]$, where m^*, ε_0 and ε_∞

denote the electronic carrier's effective mass and the material's static and optical dielectric constants, respectively. This radius is usually a few angstroms: (1) $\hbar^2/m^*e^2$ is just the Bohr radius (≈ 0.5 Å) when m^* is set equal to the free-electron mass and (2) $\varepsilon_0 \sim 5$–10 and $\varepsilon_\infty \sim 2$–3 for typical ionic solids. Thus the polaron produced with just the long-range electron–phonon interaction is generally a large polaron.

By contrast, a multi-dimensional self-trapped state formed with just the short-range electron–phonon interaction is a discontinuous function of its physical parameters. Such self-trapping is dichotomous: the carrier either self-traps with the smallest acceptable spatial extent thereby forming a small polaron or it does not self-trap at all.

Large- and small-polaron states can coexist separately when these electron–phonon interactions are combined. Alternatively combining these interactions can induce a large polaron to *collapse* into a small polaron. The confining effect of defects and the localizing tendency of disorder can also induce carriers to collapse into severely localized small-polaronic states.

A bipolaron forms when two carriers find it energetically favorable to share a common self-trapping potential well. Forming a bound state with just the long-range electron–phonon interaction requires an especially large ratio of static-to-optical dielectric constants. Even then, without correlating the positions of these two carriers to reduce their mutual Coulomb repulsion, the long-range electron–phonon interaction is unable to stabilize the self-trapping of paired carriers with respect to two separated polarons. However, the addition of the short-range electron–phonon interaction can lower the pair's energy enough to stabilize a large bipolaron. These large bipolarons are slightly smaller than a large polaron. If, however, the short-range electron–phonon interaction is too strong the bipolaron will collapse into a severely localized small bipolaron. The domain for large-bipolaron formation increases with the ratio of static-to-optical dielectric constants. In other words, large-bipolaron formation requires readily displaceable ions.

Degeneracy of carriers' electronic energy levels enhances the contribution of carrier-induced softening to bipolaron formation. A *softening bipolaron* is a singlet bipolaron whose formation is driven primarily by carrier-induced lowering of its vibrations' free energy. The four-fold orbital degeneracy of the frontier orbitals of boron carbides' icosahedra makes them prime candidates for the formation of softening bipolarons. Softening-bipolaron formation is suggested by the high density of holes which hop between icosahedra without producing a commensurate paramagnetic susceptibility, ESR or polaronic absorption but generate a large softening-type enhancement of boron carbides' Seebeck coefficients.

The very slow coherent motion of a massive large polaron is disrupted by indigenous phonons which scatter as they impinge on the region softened by the polarizable self-trapped carrier. A large polaron's hefty momentum ensures that it

will be only weakly scattered by phonons whose moderate dispersion imbues them with relatively small momenta. This weak scattering enables a large polaron to still move with a moderate mobility. A large polaron's scattering by phonons causes its mobility to fall with rising temperature as the density of these phonons increases. Concomitantly the polarons' strong scattering of indigenous phonons reduces their thermal conductivity.

Small polarons move by thermally assisted hopping with very low mobilities that increase as the temperature is raised. A small-polaron-mobility's ever steepening rise with increasing temperature culminates with Arrhenius behavior when the temperature is raised above the characteristic phonon temperature.

The Arrhenius region's activation energy generally increases as the jump distance increases. The specifics of this effect depend on (1) the range of the predominant electron–phonon interaction, (2) the spatial extent of the self-trapped carrier, and (3) pertinent phonons' dispersion. By itself, this effect, ignored by oversimplified models, promotes small polarons making short hops. Polaron hops are also restricted to nearby sites by steric constraints and by their relatively large electronic transfer energies.

Small-polarons' localized electronic states often densely fill space insuring that hopping distances are just small multiples of states' radii. The resulting electronic transfer energies are usually larger than the energies of phonons with which carriers interact. Electronic transfer is then *adiabatic*, fast enough for a carrier to transfer whenever atoms' motions afford it the opportunity. Polaron hops are often adiabatic. By contrast, *non-adiabatic* hopping occurs when electronic transfer energies are so much less than phonon energies that a carrier only infrequently transfers when atomic motion affords it the opportunity. Such small transfer energies can occur when hopping lengths greatly exceed localized states' radii. Low-temperature hopping among dopants of a very lightly doped semiconductor is generally regarded as non-adiabatic.

An adiabatic semiclassical polaron hop occurs as a carrier sloshes between the sites of a double well as it changes in response to atoms' motion. This jump-related extended motion lowers vibrations' frequencies and thereby enhances their entropy. The enhancement of vibrations' entropy is nearly proportional to the jump rate's activation energy. This relationship characterizes the *Meyer–Neldel compensation effect*. That is, the jump rate's temperature-independent pre-factor is enhanced by an entropic factor which rises exponentially with the rate's activation energy. Thus the reduction of a semiclassical adiabatic jump rate's thermally activated factor tends to be compensated by an increase of the rate's temperature-independent factor.

A carrier's hopping is usually viewed as a succession of temporally uncorrelated jumps. This picture emerges from treating hops in the non-adiabatic limit where transfers are arbitrarily rare. However, adiabatic transfers occur faster than hops'

atomic displacements form or relax. Thus a carrier's adiabatic hopping occurs in flurries. It consists of bursts of hopping activity compensated by relatively long dormant periods.

An electric current is driven as an applied electric field promotes carriers' hopping in concert with it. These hops tend to increase in length when the applied field is strong enough to overcome the rise of the hopping activation energy with jump distance. In ionic and polar materials this competition can cause the mobility's high-field activation energy to fall in proportion to the square root of the electric field thereby generating *Frenkel–Poole behavior*.

Small bipolarons form when electronic carriers self-trap as severely localized singlet pairs. However, the hopping of small bipolarons is not simply analogous to that of small polarons. Rather, small-bipolarons' carriers find it energetically favorable to break apart as they hop. This pair-breaking manifests itself in small-bipolarons' electronic transport and magnetic properties.

A polaron or bipolaron's Seebeck coefficient, the entropy transported per carrier divided by its charge, is affected by its carriers' interactions. Most generally, the change in configuration entropy arising from the addition of a charge carrier is enhanced by the narrowness of strong-coupling polaron bands. In some instances, the increase of vibrations' entropy produced by carrier-induced softening may also significantly enhance Seebeck coefficients.

The Hall mobility addresses the deflection of a moving carrier by a magnetic field. A conventional carrier's Hall mobility differs little from its drift mobility: its trap-free drift velocity divided by the electric field that drives its flow. However, the Hall and drift mobilities for a small polaron differ from one another in magnitude and temperature dependence. Moreover, the sign of the small-polaron Hall effect is often anomalous. That is, the small polaron is deflected in an opposite sense to that of a conventional carrier possessing a charge of that sign. The sign of a small-polaron's Hall effect depends on the symmetry of the self-trapped carrier's local orbital and the geometrical arrangement of sites between which it hops. Thus, Hall mobility measurements can help distinguish between a small-polaron's intrinsic hopping and a carrier's hopping between defects, impurities or dopants.

Finally, I reiterate the distinctive ideas applied to the four topics presented in the third section of this book. These subjects are (1) bipolaronic superconductivity, (2) electronic threshold switching in low-mobility semiconductors, (3) electronically stimulated desorption from surfaces, and (4) light atoms' hopping diffusion.

Similarities between the superfluidity of liquid ^{4}He and the superconductivity of electronic carriers have fueled the long-standing speculation that superconductivity can result from local singlet electron pairs which behave as mobile bosons. Here the mobile pairs are identified with large bipolarons. Large bipolarons can form within especially polarizable ionic and polar media. The electronic polarizability of large

bipolarons' self-trapped carriers promotes their softening of the vibrations to which they are coupled. The collective effect of this softening is to produce a mutual phonon-assisted attraction between large bipolarons. This mutual attraction facilitates large-bipolarons' condensation into a liquid analogous to that formed by ^{4}He. As in BCS superconductivity the stabilization of the condensed state increases with participating atoms' vibration frequencies. This scenario is suggested as an avenue to the realization of bipolaronic superconductivity.

Driving sufficiently large currents through numerous crystalline and non-crystalline semiconductors in which small-polaron formation is suspected causes them to switch from states of low conductance to states of much higher conductance. Materials having very low small-polaron-like mobilities often concomitantly possess very large carrier densities. These carrier densities will be driven still higher near interfaces with leads having higher mobility carriers as increasingly large currents are driven through them. Switching occurs when the carrier density becomes large enough to destabilize small-polaron formation with respect to electronic carriers remaining free. This scenario describes a general mechanism for electronic threshold switching.

The theory of self-trapping has been extended to address how the introduction of a delocalized electronic excitation on a surface can lead to an atom's desorption. The surface excitation's self-trapping localizes it on a surface bond, breaking the bond and releasing its atom. Depending on the magnitude of the surface excitation's kinetic energy, the process will be spontaneous or delayed by the necessity of transcending a barrier to the excitation's self-trapping.

Finally, the hopping diffusion of light atoms is treated as a generalization of the hopping of a small polaron. The physical significance of the high-temperature Arrhenius behavior's activation generally differs from that of a small polaron. The dependences of the diffusion constant's activation energy and its pre-exponential factor on a light-atom's isotopic mass provides a means of distinguishing the generalized treatment from literal application of the theory developed to describe the hopping of a self-trapped electron.

Acknowledgments

I was introduced to polarons half a century ago as a graduate student of Ted Holstein. Over time Ted and I became colleagues and close friends.

When I began to work with Ted we primarily viewed the study of polarons as an interesting academic pursuit. Many people in the condensed-matter community were unfamiliar with the concept of self-trapping and had never heard the term polaron. The idea of self-trapping received little or no mention in most introductions to solid-state physics.

It was uncertain that strong-coupling polarons were more than an oddity for which there were but a few examples. Over time reports of polaron effects grew. Evidence of polarons was reported in some transition-metal oxides, molecular solids and non-crystalline semiconductors. Experimentalists were bringing polarons to life.

Our simple models did not provide a satisfactory explanation of why these charge carriers formed polarons. It now seems that combinations of long-range and short-range electron–phonon interactions with the localizing effects of defects, impurities and disorder often trigger polaron formation.

This book offers an overview of what I have learned about polarons. Learning doesn't occur in a vacuum. I am grateful to the many people who have helped me.

I thank my collaborators for sharing work on a wide range of interesting problems. I am especially indebted to my experimental colleagues and collaborators for the data they present, the diversity of intricate materials they investigate and the questions that they and their work raise.

I was also lucky to have spent most of my career associated with Sandia National Laboratories. From my arrival in 1969 through my formal retirement I was continually able to devote myself fully to studying fundamental condensed-matter physics. My managers always supported my efforts with a sense of *noblesse oblige*. Science had not yet grown into a big enterprise.

I also appreciate the hospitality shown me by the Department of Physics and Astronomy of the University of New Mexico over the last 30 years. During this time I have collaborated with its faculty as well as its post-doctoral and graduate students. UNM has become my primary habitat since my retirement from Sandia.

For half a century I have received unflagging encouragement and support from my wife Shirley. She is remarkable in her continuing interest in learning about all of the science I study. I cannot imagine how my research and the writing of this book would have progressed without her steadfast and sensitive devotion.

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