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The genesis of polarons is often ascribed to a short paper published by Landau (Landau, 1933). That paper considers an electronic charge carrier moving slowly through an ionic solid. The carrier lingers long enough in a locale for the surrounding ions to assume shifted equilibrium positions as illustrated in Fig. 1.1. Altering the equilibrium positions of the ions establishes a potential well for the carrier. This potential well may be sufficient to bind the carrier. If the carrier's binding energy is greater than the characteristic phonon energy the bound carrier will see its potential well as nearly static. The carrier is then *self-trapped*, bound in the potential well its very presence induces. The carrier cannot escape without significant movement of the ions.

The self-trapped carrier together with the displaced ions has been defined as a strong-coupling *polaron*. The term polaron was coined in cognizance of the strong forces between a carrier and the ions of a polar material. However, the argument for self-trapping is general. As such, self-trapped carriers are reported among all classes of condensed matter. Polaron formation is energetically stable when the self-trapped carrier's binding energy exceeds the strain energy expended in displacing surrounding nuclei so as to produce the potential well that binds the carrier.

Even when the forces between the carrier and ions are too weak to produce self-trapping the carrier and the surrounding ions affect one another. The composite quasi-particle, comprising the carrier and surrounding ions whose motions are altered by the carrier's presence, is often termed a weak-coupling polaron.

Studies of self-trapping generally employ the adiabatic approach. The adiabatic method presumes that an electronic carrier adjusts to atoms' positions while also modifying atomic motion. Electronic carriers (1) shift atoms' equilibrium positions and (2) alter the stiffness constants which govern atoms' harmonic motions.

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Fig. 1.1 An excess electron (hatched area) held on a cation shifts the equilibrium positions of the surrounding anions (filled large circles) and cations (filled small circles) from their carrier-free positions (open large and small circles). These shifts of ions' equilibrium positions produce a potential well for that carrier.

Strong-coupling polarons primarily shift atoms' equilibrium positions whereas weak-coupling polarons modulate atoms' vibration frequencies.

Adiabatic studies of self-trapping explicitly demonstrate that self-trapping is a nonlinear phenomenon. In particular, the self-trapping potential depends on the wavefunction of the self-trapped carrier. As a result, the nature of the self-trapped state depends critically on the details of the interaction between a carrier and the surrounding medium. For example, the spatial extent of a self-trapped state varies continuously with material parameters when the carrier interacts with the ions of a polar medium solely via the long-range Coulomb interaction. By contrast, the self-trapped state collapses to the smallest possible physical unit when the interaction between a carrier and the atoms is only via the short-range interaction characteristic of a covalent solid.

Self-trapping becomes more intricate in real solids for which a carrier's interactions with its surroundings have both long-range and short-range components. Molecular solids permit several types of molecular polaron. All told, self-trapping is sensitive to a material's anisotropy and its disorder. Localizing, constraining or slowing a carrier all foster its self-trapping.

A strong-coupling polaron is identified by its distinctive properties. A strongcoupling polaron possesses an absorption produced by optically exciting its selftrapped carrier. These phonon-broadened absorption bands are akin to those of trapped carriers. Since a self-trapped carrier can move only when the involved atoms move, a strong-coupling polaron must move very slowly. Concomitantly, its CAMBRIDGE

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energy band is narrower than the characteristic phonon energy and its effective mass is correspondingly large.

Strong-coupling polarons manifest two distinct types of transport properties. A *large polaron* extends over several structural units and thereby moves with a coherence length exceeding the characteristic inter-site separation. The very heavy mass of such a polaron can lead to its being only weakly scattered by phonons. This weak scattering can compensate its large mass to yield a mobility ($\gg1$ cm²/V-sec) that falls with increasing temperature.

A *small polaron* is confined on a single structural unit and typically moves incoherently. A carrier's motion is then usually described as occurring via a succession of occasional phonon-assisted jumps between adjacent sites. The small-polaron hopping mobility is generally very low, $\ll 1 \text{ cm}^2/\text{V-sec}$, and rises with increasing temperature. A distinguishing feature of such incoherent motion is the occurrence of Hall-effect sign anomalies. In these instances a small polaron is deflected by a magnetic field in the opposite direction than a classical particle of the same sign. Figure 1.2 summarizes the relationships between different types of polaron along with their principal characteristics.

Polarons interact with one another through several effects. Same-signed selftrapped carriers repel one another through their mutual Coulomb repulsion. Polarons also interact with one another through the interference of their patterns of atoms' shifted equilibrium positions and vibration frequencies. These interference effects can result in attractive interactions through which like-signed polarons may find it energetically favorable to pair as *bipolarons*.

Interactions among polarons and bipolarons also foster their collective behavior. Large polarons and bipolarons may be able to flow collectively as a liquid. Alternatively, polarons and bipolarons can order in a manner that is commensurate with the underlying lattice structure resulting in their being pinned and unable to flow. In addition, increasing the density of carriers tends to diminish their ability to self-trap as they compete to displace the same atoms. Driving the carrier density high enough can thereby destabilize carriers' self-trapping. Switching between different situations underlies various polaron-related phase transitions. These phases can be electrical insulators, small-polaron semiconductors, metals and even perhaps superconductors.

Measurements of optical, magnetic and electronic transport properties indicate polarons in a wide range of condensed matter. These materials include (1) ionic solids such as KCl, (2) magnetic insulators such as MnO, (3) molecular solids such as S_8 , (4) many glasses (e.g. transition-metal-oxide glasses) and (5) liquids such as water in which electronic carriers are *solvated*. This book will describe how different types of polaron form and the properties through which they can be identified.

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Fig. 1.2 Essential characteristics of a weak-coupling polaron and the two types of strong-coupling polaron, a large polaron and a small polaron, are summarized. A self-trapped carrier is bound with energy E_{binding} in the potential well produced by shifts of surrounding atoms' equilibrium positions. Self-trapping occurs when the bound carrier's electronic frequency E_{binding}/h exceeds these atoms' characteristic vibration frequency v. Optical excitation of the self-trapped carrier produces an absorption band. The mass associated with an elementary translation of the unit comprising the self-trapped carrier and its pattern of displaced atomic equilibrium positions m^* usually greatly exceeds the mass of an unbound carrier m. The polaron is deemed large when the spatial extent of its self-trapped carrier R_p exceeds the lattice constant a. A large polaron generally moves coherently with a moderate mobility μ which falls with increasing temperature. By contrast, a polaron usually moves incoherently via phonon-assisted hopping with a very small mobility which increases with increasing temperature.

The polaron problem has been extended to apply to other situations in which an agile entity interacts with its relatively sluggish environment. For instance, the polaron approach has been employed to address the interaction of an exciton with surrounding atoms. Light interstitial atoms (e.g. hydrogen and its isotopes) diffusing among the relatively heavy atoms of a metal has been treated as a generalization of small-polaron hopping. The concept of a magnetic polaron arises from considering the interaction of a carrier with the localized magnetic moments of a magnetic insulator. Moreover, a carrier in a magnetic solid also generally interacts with its

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atomic displacements. Synergy between the effects of a carrier's interactions with magnetic moments and atomic displacements is evident as misalignment of local moments triggers the collapse of a carrier into a small polaron. Magnetic and electronic transitions are thereby linked. These extensions of the polaron problem are also discussed here.

Part I

Polaron Formation

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Electron-phonon interactions

Electron-phonon interactions describe how the energy of an electronic charge is affected by alterations of the positions of the atoms of the encompassing medium. Polaron problems usually take a charge carrier's energy to depend linearly on shifts of nuclear positions. Here, for simplicity, the medium is represented as a continuum. Then the net effect of deforming the continuum by $\Delta(u)$ at positions designated by u is to shift the effective potential energy of a carrier at r by

$$V(\mathbf{r}) = \int d\mathbf{u} Z(\mathbf{r} - \mathbf{u}) \Delta(\mathbf{u}), \qquad (2.1)$$

where Z(r - u) defines the magnitude and range of the electron-phonon interaction.

2.1 Long-range electron-phonon interaction

Ionic and polar materials support a long-range component of the electron-phonon interaction. Pairing anions with cations enables the Coulomb potential of these materials to be represented as that from an array of electric dipoles. Altering the separation between the ions of a dipole shifts the potential seen by a carrier. The modulation of the carrier's potential energy at r due to altering the charge separation of a dipole centered at u is governed by

$$Z_{\rm LR}(\boldsymbol{r}-\boldsymbol{u}) \equiv -\frac{\sqrt{\frac{e^2}{4\pi} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0}\right) \frac{k}{V_{\rm c}}}}{|\boldsymbol{r}-\boldsymbol{u}|^2} \cos\theta, \qquad (2.2)$$

where (as illustrated in Fig. 2.1) θ is the angle between the electric dipole and the vector $\mathbf{r} - \mathbf{u}$. The constants in Eq. (2.2) are the carrier's charge e, the material's

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Fig. 2.1 An electric dipole (dotted arrow) directed along the vector from the carrier's centroid u interacts with its charge (hatched area) at r.

optical and static dielectric constants ε_{∞} and ε_0 , the Hooke's law stiffness constant for the electric dipole's charge separation k, and the unit cell volume V_c . This combination of physical parameters relates a modulated electric dipole to the polarization-adjusted electric potential that it produces.

A material's dc polarization is proportional to $1 - 1/\varepsilon_0$. This polarization contains contributions from displacing electrons as well as from displacing relatively massive and slow-moving ions. By comparison the optical polarization $1 - 1/\varepsilon_{\infty}$ only contains contributions from electrons since only they can move fast enough to follow a highfrequency oscillating electric field. Thus, $1/\varepsilon_{\infty} - 1/\varepsilon_0$ measures the slow polarization arising from displacing ions. This difference of the reciprocal of the dielectric constants tends to be small for covalent materials since there $\varepsilon_0 \approx \varepsilon_{\infty}$. Hence the associated long-range electron–phonon coupling also tends to be small for covalent materials. By contrast, the long-range electron–phonon coupling is of major importance in ionic crystals such as alkali halides when $\varepsilon_0 \approx 2\varepsilon_{\infty}$. The long-range electron– phonon coupling is exceptionally strong in ferroelectric and extremely polar materials as they are characterized by $\varepsilon_0 \gg \varepsilon_{\infty}$.

The potential well produced by ions' relaxation about a static point charge is a useful fiducial situation when discussing self-trapping. Ions assuming shifted equilibrium positions in response to the presence of the static point charge produce a Coulomb-like well

$$V_{\rm eq}^{\rm LR}(\mathbf{r}) = -\left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0}\right) \frac{e^2}{|\mathbf{r}|}.$$
 (2.3)

The magnitude of this Coulombic potential measures the strength of the long-range electron–phonon interaction. The potential well generated by the long-range electron–phonon interaction about a confined carrier of radius R is schematically illustrated in Fig. 2.2. As discussed in Section 4.3, the well depth is proportional to 1/R.