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SMALL BIPOLARONS IN BORON CARBIDES: PAIR BREAKING IN SEMICLASSICAL HOPPING*

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1. INTRODUCTION

A pair of charge carriers can be bound within a common potential well produced by displacing atoms from their carrier-free equilibrium positions. These two self-trapped carriers together with the associated atomic-displacement pattern is referred to as a bipolaron. If the self-trapped carriers' wavefunction is primarily confined to a single structural unit (atom, bond or molecule), the bipolaron is termed small. If however the self-trapped carriers' wavefunction extends over multiple structural units, the bipolaron is called large. Small bipolarons form in crystals if the energy lowering due to the carriers' self-trapping exceeds the electronic-transfer energy associated with an electronic carrier's intersite motion.¹⁾ Small-polaron and -bipolaron formation is also often induced by disorder.²⁾

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Interest in bipolarons focuses on situations in which they are energetically stable with respect to dissociating into two individual carriers. Stability is achieved when the additional lowering of the atomic-displacement-related energy arising from two carriers sharing a common site overwhelms their mutual Coulomb repulsion. The Holstein-Hubbard model provides a simple representation of small-bipolaron formation. In this model, carrier-stabilized shifts of atomic equilibrium positions double when two carriers reside on a common site. In addition, the bipolaron's two carriers experience a mutual on-site Coulomb repulsion of U . As a result, the groundstate energy of a small bipolaron comprising two carriers of a singlet that share a common spatial state is $-4E_b + U$ when $-2E_b$ is the groundstate energy of two separate small polarons. Small-bipolaron formation is stable when $2E_b > U$.^{3,4)}

Self-trapped carriers only move when the positions of the atoms whose displacements produce self-trapping change. When atoms move so as to shift small-polaronic self-trapped carriers between adjacent sites, changes of the self-trapped carriers' energies always exceed their intersite electronic transfer energy. Since small-polaronic self-trapped carriers thereby lose coherence as they move, their transport is described as hopping incoherently between localized states.

2. BORON CARBIDES

In this section I first describe boron carbides. I then describe the chemical basis of small-bipolaron formation in boron carbides. Finally, I enumerate features of boron carbides that make them ideal for studying small-bipolaron hopping motion.

Boron carbides are based on boron-rich clusters in which each of twelve atoms resides at a vertex of an icosahedron. Each atom of the cluster has one of its electrons involved in a covalent bond that links the cluster to an outside atom. The remaining second-shell electrons of icosahedral atoms are delocalized on the

surface of the icosahedron. A pure boron icosahedron, such as occurs in the borane molecule, $B_{12}H_{12}$ (in which each boron atom is bonded to a hydrogen “tie-off” atom) has a bielectron affinity: $B_{12}H_{12} + 2e \rightarrow (B_{12}H_{12})^{2-}$. Boron-rich icosahedra in solids also have a strong affinity for two electrons. In boron carbides the two electrons that boron icosahedra desire are obtained from two sources. First, carbon substituting for boron in an icosahedron provides one extra electron to it. Second, icosahedra receive electrons donated by non-icosahedral structural units. Boron carbides’ electron-donating structures are CBC chains that lie on the longest diagonals of rhombohedra having icosahedra at their corners.

Boron carbides exist with carbon concentrations between about 9 and 19 atomic percent carbon. These carbon concentrations provide too few electrons to satisfy all icosahedra’s need. As a result, some icosahedra have bipolaronic holes. Boron carbides’ p-type bipolarons are $(B_{11}C)^+$, carbon-containing icosahedra that lack two of the electrons needed to fulfill their internal bonding requirements.⁵⁾

As the carbon concentration is reduced from 19 % to 13 % the concentration of bipolaronic holes per icosahedron rises from near 0.1 to about 0.5. Reducing the carbon concentration from 13 % to 9 % introduces B_{12} icosahedra in place of $B_{11}C$ icosahedra. Because B_{12} icosahedra lack the positive charge of a carbon nucleus, their empty orbitals are much higher in energy than those of [isoelectronic] $(B_{11}C)^+$ icosahedra. Therefore, below 13 % carbon, bipolaronic holes occupy about 0.5 of the $B_{11}C$ icosahedra and avoid B_{12} occupancy.

Several features of boron carbides make them desirable systems for studying hopping conduction. The locations of the carriers are known: $B_{11}C$ icosahedra that reside at the corners of a simple rhombohedral lattice. The carrier density is controlled by the carbon content and is large enough, about 10^{21} cm^{-3} , to overwhelm extrinsic effects. The carrier density is large enough to permit

transport measurements down to below 10 K while boron carbides' high melting temperature has permitted transport to be studied up to 2400 K.

3. BIPOLARONS AND SMALL-POLARONIC HOPPING

Above 100 K boron carbides' conductivity and Hall mobility approach the thermally activated behavior expected of small-polaronic hopping.⁶⁾ The conductivity's activation energy, 0.16 eV, is nearly independent of carbon concentration. The conductivity scales with the carrier concentration, peaking near 13 % carbon. Magnetic susceptibility measurements indicate far fewer spins (10^{19} cm^{-3}) than carriers (10^{21} cm^{-3}).⁷⁾ These results imply that most carriers pair as singlet small bipolarons and transport occurs via phonon-assisted hopping.

With a concentration of c_b stable singlet small-bipolarons, the thermal population of small polarons is $c_p \equiv 2[c_b(1 - c_b)]^{1/2} \exp[-(E_b - U/2)/k_bT]$. Recent ESR studies by O. Chauvet (EPFL) on materials produced by T. L. Aselage (Sandia) found that above 100 K boron carbides' spin density rises in an activated manner (activation energy ≈ 0.1 eV) above that of defects' spins. This observation prompted this author to ask: Do a small bipolaron's two carriers hop jointly or do they hop sequentially: one hops and then the other follows? How does the conductivity of thermally available small polarons compare with that of small bipolarons?

To answer these questions, the rates for semiclassical charge transfer in a system in which it is energetically favorable for carriers to form small bipolarons were calculated. Five charge transfer processes were considered: 1) the two charge carriers of a singlet small bipolaron hop jointly, 2) a singlet small-bipolarons' carriers separate as only one of them hops, 3) one of two adjacent small polarons hops so as to merge into a bipolaron, 4) one of a bipolaron's two carriers hops to an adjacent site occupied by a small polaron, 5) a small polaron hops to a vacant site. The fourth and fifth processes have the same rate, leaving four distinct rates:

$$R(\text{joint}) = v \exp[-(2E_b - |t_2|)/k_B T] P_2(T), \quad (1)$$

$$R(\text{separate}) = v \exp[-(2E_b - U + U^2/8E_b - |t_1|)/k_B T] P_1(T), \quad (2)$$

$$R(\text{merge}) = v \exp[-(U^2/8E_b - |t_1|)/k_B T] P_1(T), \quad (3)$$

$$R(\text{single}) = v \exp[-(E_b/2 - |t_1|)/k_B T] P_1(T), \quad (4)$$

where v is the characteristic vibrational frequency. The magnitude of the electronic transfer energy for collateral motion of two electronic changes, t_2 , is smaller than that for a single electron, t_1 : $t_2 \approx t_1 S$, where S is the intersite overlap factor, $S \ll 1$. $P_1(T)$ and $P_2(T)$ are the one- and two-electron transfer factors, respectively. For small electronic transfer energies, $P_1(T)$ and $P_2(T)$ are respectively proportional to the square of t_1 and t_2 . However, for large enough transfer energies (typically exceeding a phonon energy), “adiabatic” hopping, $P_1(T)$ and $P_2(T)$ saturate at ≈ 1 . Thus, $|t_1| > |t_2|$ and $P_1(T) \geq P_2(T)$. Then, with bipolaron stability, $2E_b > U$,

$$R(\text{merge}) \geq R(\text{single}) \geq R(\text{separate}) > R(\text{joint}). \quad (5)$$

Collateral hopping of a small bipolaron's two electrons, $R(\text{joint})$, produces the slowest of these rates. The fastest rate is that for the merger of two adjacent polarons into a small bipolaron, $R(\text{merge})$. Thus, sequential small-bipolaron hopping, in which carriers repeatedly separate and then merge, occurs with a rate $\approx R(\text{separate})$. Small polarons can also escape merger by one of them hopping away from the other at the rate $R(\text{single})$. The resulting individual small polarons move faster than can a bipolaron by either the collateral or sequential motion of its carriers, $R(\text{joint})$ or $\approx R(\text{separate})$, respectively. The presence of small bipolarons

does not impede the motion of a small polaron because the rate for the transfer of one of a small bipolaron's carriers to an adjacent small polaron is also $R(\text{single})$.

The conductivity for this semiclassical hopping has been estimated as being the sum of contributions that each are the product of one of the above transfer rates and the thermodynamic probability of an appropriate (initial) configuration of small-polarons, small-bipolarons and vacant sites occurring. This conductivity is always dominated by the rapid hopping of the relatively few carriers that remain small polarons rather than being paired as small bipolarons: $\sigma \cong (e^2/ak_B T) c_p R(\text{single})$, where e is the electronic charge and a is the intersite separation. The relative contribution of small-polaron hopping to the conductivity grows as the small-bipolaron stabilization energy, $2E_b - U$, is increased.

Semiclassical hopping prevails at temperatures that typically exceed about 1/3 the "temperature" of the phonons that couple most strongly to the carriers. However, at low enough temperatures, small-polaronic hopping is dominated by process that involve atomic tunneling. Then, small-polaronic hopping becomes non-Arrhenius and joint hops of small-bipolarons' two carriers come to dominate conduction.

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