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Solvated polaron in an ionic lattice

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It is shown that an electron in an ionic lattice having unit cells sufficiently large to accommodate water molecules forms very weakly bound polarons centered around clusters of water molecules. Consequently, electrons can hop between these clusters, initiating a novel mode of electronic transport.

It is well known that the freedom of motion of an electron through an ionic lattice is restricted by the formation of polarons.[1-5] The deformation of the lattice by the electric field traps the electron into a potential hole. The force on the electron resulting from this effect can be deduced by the following method.[1-5] If the electron is at rest inside the lattice, the energy of its electric field is $e^2/2r\epsilon_{IE}$, where r is the radius of the polarization cavity and ϵ_{IE} is the static dielectric constant of the crystal originating from ionic and electronic polarizabilities. If the lattice was not deformed the field energy would be $e^2/2r\epsilon_E$, where ϵ_E is the optical dielectric constant depending purely on electronic polarizabilities. Thus the reduction in energy due to strain in the lattice is

$$\Delta B = \frac{e^2}{2r}\left(\frac{1}{\epsilon_E} - \frac{1}{\epsilon_{IE}}\right) . \tag{1}$$

The energy given by (1) may be viewed as resulting from a Coulomb-like force[1-5]

$$\frac{e^2}{r}\left(\frac{1}{\epsilon_E} - \frac{1}{\epsilon_{EI}}\right) \tag{2}$$

directed towards the center of deformation. The energy of the trapped electron can assume quantized values or when the effective mass is large[6,7] (small polaron), (1) gives the binding energy.[1-5]

In this Brief Report it is shown that in the presence of clusters of absorbed water molecules within a solid, electrons can easily hop between these clusters. The screening of the electron's field by water molecules greatly reduces the binding energy of electrons to the lattice near a cluster.

Experimental data on electrical transport in Prussian blue (an ionic crystalline material of large lattice constant that accommodates water molecules within the interstices) are presented as a possible practical situation in which this phenomenon is realized.

In the presence of a background of water molecules, the static dielectric constant ϵ_{IE} in (1) must be replaced by ϵ_{WIE}, which is the dielectric constant including total polarizability γ_W of H_2O molecules, ionic polarizability γ_I of the lattice, and the electronic polarizabilities γ_E of the constituents of the lattice. From the Clausius-Mossotti relation[8]

$$\epsilon_{WIE} = \frac{1 + (8\pi/3)(N_W\gamma_W + \Sigma_i N_{Ii}\gamma_{Ii} + \Sigma_i N_{Ei}\gamma_{Ei})}{1 - (4\pi/3)(N_W\gamma_W + \Sigma_i N_{Ii}\gamma_{Ii} + \Sigma_i N_{Ei}\gamma_{Ei})} , \tag{3}$$

where $N_W =$ concentration of water molecules and N_{Ii}, N_{Ei} concentrations of the relevant entities in the lattice of the ith type. Again for the solvated polaron the constant ϵ_E in (2) must be replaced by ϵ_{WE} which includes all contributions to ϵ except ionic polarizabilities that causes deformation of the lattice, i.e.,

$$\epsilon_{WE} = \frac{1 + (8\pi/3)(N_W\gamma_W + \Sigma_i N_i\gamma_{Ei})}{1 - (4\pi/3)(N_W\gamma_W + \Sigma_i N_i\gamma_{Ei})} . \tag{4}$$

γ_I and γ_E are generally small, compared to γ_W; thus it is evident from (3) and (4) that, because of the high polarizability of water, at sufficiently high concentrations of H_2O molecules (i.e., as in liquid water) the difference between ϵ_{WIE} and ϵ_{WE} can be vanishingly small. Therefore, the binding energy of the solvated polaron can be negligible. Since the contribution from electronic polarizability to ϵ is small, using (3), (4), and the Clausius-Mossotti relation for the optical dielectric constant ϵ_E of the pure material the polaron binding energy can be put in the form

$$\Delta B = \frac{e^2}{2r}\left(1 + \frac{2(\epsilon_{WE} - 1)}{(\epsilon_{WE} + 2)}\right)^{-1}\left(\frac{\epsilon_E - 1}{\epsilon_E + 2}\right) . \tag{5}$$

Also without much error ϵ_{WE} in (5) can be replaced by ϵ_W the static dielectric constant of water. Conduction occurs by hopping of electrons between the clusters of water molecules. At higher temperatures, i.e., $kT \sim$ energy of a hydrogen bond, the clusters break and the phenomenon disappears.

We have used a continuum theory on an atomic scale. This approximation is reasonably valid when the number of molecules involved is fairly large.

As one possible example, we consider electrical transport in Prussian blue. Solid Prussian blue ($Fe_4[Fe(CN)_6]_3$) whose crystal structure, extensively investigated by many workers, is known to consist of a face-centered-cubic lattice[9-11] (unit cell length $\simeq 5.1$ Å) of alternating Fe^{2+} and Fe^{3+} ions, with cyanide ions placed along the edges of the cubes. The material can absorb as much as 2–3 molecules of H_2O per unit cell. The static dielectric constant of the anhydrous solid is $\simeq 4.7$. The optical dielectric constant estimated from determinations of the Brewster angle[8] or calculations based on known electronic polarizabilities of the constituents is $\simeq 1.4$. Thus the binding energies of polarons solvated and unsolvated calculated from (2) and (7) are ~ 0.7 and 0.06 eV, respectively.

Temperature variation of the conductivity of anhydrous

Prussian blue is indicated in Fig. 1(a). The plot of lnσ vs T^{-1} fits into a straight line showing that the relation

$$\sigma = \sigma_0 e^{-E/kT} \tag{6}$$

is satisfied with activation energy $E = 0.76$ eV. The conductivity is strongly enhanced in the presence of absorbed interstitial water. Figure 1(b) gives a plot of lnσ vs T^{-1} for a sample containing ~8% of H_2O by weight (on average 0.9 molecules per unit cell). The activation energy here is very much smaller ~0.08 eV. Another interesting feature is the sudden increase in the slope of the plot at $T = T_c \sim 101\,°C$. Possibly the cluster is more effective in screening the electric field of the electron, when H_2O molecules are hydrogen bonded to each other as in liquid water. These bonds break at the transition temperature T_c; $kT_c \simeq 0.03$ eV is of the order of magnitude of a hydrogen bond. The optimum amount of water that the solid can accommodate is 2–3 molecules per unit cell. Thus, compact clusters can be formed quite easily and each cluster may involve several cells. When the concentration of water is decreased from ~8%, E changes continuously, as well as in a stepwise manner.[12,13] Here the mechanism is probably more involved.[12,13] The point we want to stress is that the magnitudes of maximum and minimum observed activation energies are of the same order as the values predicted for the binding energies of unsolvated and solvated electrons. It is important to note that with the presence of water at concentrations discussed here, the ionic conduction in Prussian blue is negligible or absent. This can be proved by passing large currents through thin disks of the pressed material, when the absence of electrolytic effects rules out ionic conduction.

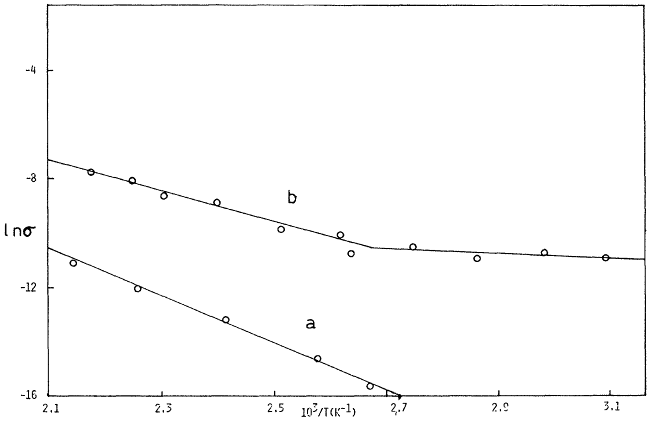

FIG. 1. Plot of lnσ ($\Omega^{-1}m^{-1}$) for Prussian blue (a) anhydrous, and (b) containing ~8 at.% H_2O (~0.9 molecules per unit cell).

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