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Letter to the Editor

Is there a 'native' band gap in ion conducting glasses?

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Abstract

It is suggested that the spectrum of ion site energies in glasses exhibits a 'band' gap, thus establishing an analogy between ion conducting glasses and intrinsic semiconductors. This implies that ion conduction (as in crystals) takes place via vacancies and interstitial ions.

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Ion conduction in glasses has been studied for many years but there is still no universally accepted theory [1–8]. Some theories assume a more or less collective conduction mechanism, others assume that conduction proceeds via defects like vacancies or interstitials. We shall argue that most likely the latter is always the case. The approach taken below is to consider the very basic questions which may be asked.

The obvious first question relates to ion statics:

- *What is the nature of the states of the ionic system?*

It is quite clear that any glass has a discrete number of possible ion sites and that each ion site has room for just one ion (ions have a substantial volume, moreover there are Coulomb repulsions between ions); as pointed out by Kirchheim and Stolz long time ago [9] an important consequence is that mobile ions behave like Fermions from the statistical mechanical point of view [10,11]. It is also clear that ionic motion takes place via transitions between different distributions of the mobile ions among the available sites.

The next question is:

- *What is the nature of the individual ion sites?*

Following the commonplace assumption in most previous works we shall assume that the ions do not significantly perturb the network (the dynamic structure model of Bunde et al. [12], of course, challenges this assumption). Given a rigid network there are two possibilities, depending on the strength of the interactions between mobile ions relative to ion–lattice interactions. If interactions among mobile ions are relatively weak, each ion site has a well-defined energy ϵ which does not depend on whether or not neighboring sites are occupied. In this case the energy of the ionic system is simply the sum of all mobile ion energies.

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We shall initially assume that [mobile] ion–ion interactions are indeed relatively weak, but later on remove this limitation.

The density of ion site energies is denoted by $p(\epsilon)$. The spread of energies deriving from the disorder of the glassy matrix is expected to be much larger than k_BT. Consequently, to a good approximation the following picture applies: States up to an energy ϵ_F are filled while states above ϵ_F are empty. ϵ_F is the so-called Fermi energy. As is well-known from the theory of electronic conduction in solids [13] there are two possibilities: $p(\epsilon_F) > 0$ corresponds to the Fermi energy lying within an energy band ('metal'), while $p(\epsilon_F) = 0$ corresponds to having the Fermi energy placed between two bands, i.e., the existence of a band gap $\Delta > 0$ ('semiconductor'). The 'metal' case was first treated by Kirchheim [14] and more recently by Baranovskii and Cordes [10] and Maass [11]. We argue below that it is more realistic to assume the existence of a band gap.

To be specific, consider the case of an ordinary alkali-oxide glass. The glassy network is created when the melt solidifies at the glass transition. The number of ions is equal to the number of negatively charged non-bridging oxygen (NBO) atoms. Because of Coulomb attraction it is favorable for each NBO atom to have at least one ion site associated with it. The crucial question is whether there are *more* low-energy ion sites than the number of NBO atoms. Any empty low energy site is basically a hole in the network structure. If there were a substantial fraction of holes, the density of the glass would be considerably lower than the density of crystals of similar composition. This is never the case. We conclude that there is only one low energy site per mobile ion, one per NBO atom. This implies the existence of a band gap.

An alternative argument for the existence of a band gap considers the annealing state of the glass. If the glass is well annealed, all atoms *including the ions* have been gradually and delicately brought into low-energy states defined by surrounding atoms. It is then highly unlikely that there are more low-energy ion sites than the actual number of ions. Surely, the glass would have to spend energy to produce empty sites carefully optimized for housing an ion, energy spent without reaping any benefits. This is like spending a lot of effort preparing for a guest that in the end prefers to stay elsewhere!

We have arrived at the following picture:

> *An ion conducting glass has 'native' ion sites, the number of which is equal to the number of ions. There are also 'non-native' ion sites in the glass, but these all have energies at least the band gap Δ higher than that of any native site.*

This picture is implicit already in the 1985 paper by Kirchheim and Stolz on tracer diffusion and mobility of interstitials in disordered materials [9] (cf. Fig. 10).

Proceeding to consider the conduction mechanism, we shall refer by analogy to the theory of electronic conduction in semiconductors [13]. A semiconductor has two sorts of charge carriers, *electrons* excited into the conduction band and *holes* of opposite charge (these are simply electrons missing from the valence band). In an intrinsic semiconductor – the analogue of the ionic glass – the number of mobile electrons is equal to the number of holes. For the ionic glass the analogue of a hole is a vacancy and the analogue of an excited electron is an interstitial ion, i.e., an ion placed in one of the high energy sites unoccupied in the 'ground state' of the ionic system. At any given time the number of vacancies is equal to the number of interstitial ions.

If $\Delta \gg k_BT$, as is assumed from here on, the number of both vacancies and interstitial ions is much lower than the number of mobile ions and interstitial sites. In this situation charge transport proceeds via motion of well-defined vacancies and interstitial ions. These are 'quasi-particles' with only finite lifetime, but at the low quasi-particle concentrations guaranteed by $k_BT \ll \Delta$ their lifetimes are long compared to typical jump times: Just as in semiconductors quasi-particles are created in pairs, move away from each other, and end their life by annihilating. The annihilation is a recombination where an interstitial ion jumps into a vacancy. In most cases the ion and vacancy annihilating are not the same as those originally created in a pair (note that, if they *are* the same, the entire process has not resulted in any charge transport).

The final question is:

- *How do vacancies and interstitial ions move?*

Consider a vacancy. To move it should be filled by an ion. This ion either comes directly from another native site, or via one or more stops at interstitial sites. If v is a vacancy and i is an interstitial ion, the 'direct' mechanism is symbolized

$$v \to v,$$

while the second mechanism, because the first ion jump creates a vi pair, is

$$v \to vvi \to \cdots \to vvi \to v.$$

At low ion concentrations only the indirect mechanism is realistic.

Because of the complete symmetry between vacancies and interstitial ions we can immediately write up the two possible mechanisms for interstitial ion movement: The 'direct' mechanism is

$$i \to i,$$

the 'indirect' is

$$i \to iiv \to \cdots \to iiv \to i.$$

So far we have assumed that interactions between mobile ions are weak, corresponding to low mobile ion concentration. It is likely, however, that the above picture applies in general: Because the glass is prepared from the liquid by gradual cooling, the entire ion + glass system has low energy, even for large ion concentrations. In contrast to the dilute case each native ion site energy now has substantial Coulomb contributions from neighboring mobile ions. Nevertheless, it is still to be expected that it takes considerable energy to move an ion out of its native site, simply because the entire system minimized its energy during the glass transition. Note the consistency of the picture: If there *is* a band gap, the vast majority of mobile ions are to be found at their native site, so the contribution to the native site energy from neighboring mobile ions is there basically all time.

What are the consequences of the proposed picture? Annealing a glass lowers its energy. One thus expects that the native ion sites lower their energy, while the energy of interstitial sites is expected to increase because the structure becomes more tight. Annealing thus increases the band gap. This implies a lowering of the conductivity, as always seen in experiment. Another consequence relates to our understanding of conductivity which is basically charge carrier density times mobility. The analogy to intrinsic semiconductors tells us that there are two types of charge carriers with same density, but not necessarily same mobility. The mobility is measured, e.g., by Hall effect experiments. If the vacancy mobility exceeds that of the interstitials one would see a sign change in the Hall effect. If vacancies and interstitials have same mobility there should be no Hall effect. Finally, we note that it is possible via correlation factor measurements to distinguish between vacancy and interstitial mechanism [15,16], in other words: determine which of the two has the largest mobility. For the glass of the composition $Na_2Si_2O_5$, for instance, it is concluded that ion conduction proceeds via interstitials, not vacancies [15].

To summarize, referring to the fact that glass is produced from liquid we arrive at a picture of glass ion conduction as proceeding via vacancies and interstitial ions. This idea is not new, of course [3,5,17], but has here been discussed as a direct consequence of the existence of a band gap. Recent computer simulations by Cormack and coworkers and by Heuer and coworkers [18,19] are consistent with this picture.

Conclusion: Ionic crystals trivially have a 'native' band gap. We suggest that this is also the case for ionic glasses.

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