Ionic Conductivity and Disorder Modes in Borate Glass Systems

A. Avogadro, S. Manzini, and M. Villa
Istituto di Fisica "A. Volta" e Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Via Bassi 6, 27100 Pavia, Italy

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It is shown that ionic conductivity in $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$ amorphous compounds is describable as a coupling between disorder modes of glass-forming borate units and Ag^+ translational degrees of freedom. A model is presented for the ionic conductivity where ions and disorder modes are represented by two pseudospin variables which interact through an exchange term. This model, as applied to the interpretation of conductivity activation energies and prefactors in borate glass systems, is discussed.

A number of glasses have recently been discovered with ionic conductivities up to $10^{-1}\ \Omega^{-1}\ cm^{-1}$ at room temperature.[1] We have investigated the ionic transport in quenched $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$ by comparing ionic conductivity[2] and NMR results.[3] We found evidence of a new ionic-conductivity mechanism in glasses that will be discussed in this paper.

The most relevant experimental facts that we observed are the following:

(1) The ^{11}B central line is very similar to the narrow component of the boron spectrum in the binary $Ag_2O \cdot B_2O_3$ system.[4] This component has been assigned to BO_4 tetrahedral units.[5] It is also independent of the composition in the glass-forming region ($0 \leq x < 0.8$). No broad or structured components typical, for example, of the BO_3 groups[4,5] have ever been observed in the quenched glasses.

(2) The ^{11}B spin-lattice relaxation time (T_1) as a function of temperature goes through a minimum.[3] The temperature of the minimum (T_{min}), depends on the Larmor frequency (ω_L) and increases when x is decreased. At $\omega_L = 1.26 \times 10^8\ sec^{-1}$, T_{min} values are in the 200–450 K range. For all compositions, T_{min} decreases by 15 ± 5 K when the frequency is decreased to $\omega_L = 6.91 \times 10^7\ sec^{-1}$.

If we assume that, for $x > 0.1$, the major contribution to the dc conductivity comes from Ag^+ ions bound to the iodine, the Nernst-Einstein relation yields an Ag^+ diffusion coefficient at T_{min} of 10^{-8}–$10^{-9}\ cm^2\ sec^{-1}$ from which jump frequencies of the order of ω_L can be estimated with the random-walk formula. However, the relaxation rates at T_{min} cannot be explained as a direct effect of the diffusing charges for the following reasons: (i) The boron atoms are shielded from the moving ions by the oxygens and even under the most favorable circumstances the Cohen and Reif model[6] of quadrupolar relaxation by a charged defect fails to predict the order of magnitude of the experimental T_1. (ii) The values of T_1 at the minimum do not follow the Cohen and Reif result $T_1 \propto x^{-1}$. (iii) A frequency-dependent minimum in T_1 also occurs in the glass with nominal composition $Ag_2O \cdot B_2O_3$. We can conclude that the changes of the electric-field-gradient components responsible for T_1 are related to internal motions of the BO_4 groups. Whether these motions are deformations or hindered rotations of the tetrahedra, we may classify them as "disorder modes" to indicate that they have a large amplitude and/or a low frequency when compared with the vibrational modes typical of crystals. Displacements of the T_1 minima with ω_L suggest that the motion responsible for T_1 at the minimum takes place with an activated rate ω_B, i.e.,

$$\omega_B = \omega_0 \exp(-E_B/RT). \tag{1}$$

The fundamental frequency ω_0 is expected to fall in the range of the BO_4 vibrational frequencies[7] (800–1500 cm^{-1}) in the Ag_2O-B_2O_3 glass system. If one assumes $\omega_0 = 3 \times 10^{13}\ sec^{-1}$ and $\omega_B \simeq \omega_L$ at T_{min}, the T_1 data give E_B for the explored composition range. Changes of ω_0 in the interval 800–1500 cm^{-1} cause modifications of E_B of less than $\pm 3\%$. Figure 1 compares the activation energies for the BO_4 motion E_B with the ones for Ag^+ diffusion E_A. The experiments indicate that the translational degrees of freedom of the ions and disorder modes typical of glasses are strongly coupled.

To discuss this coupling, we will introduce an exchange-type model Hamiltonian. We will represent the mobile ion with a two-value pseudospin variable a to describe the ion in the ground or vibrational state ($a = 0$) and in the excited or diffusional state ($a = 1$). Similarly, $b = 0$ and $b = 1$ will indicate that the structural borate unit is in an equilibrium configuration and moving among configurations, respectively. Fermion creation

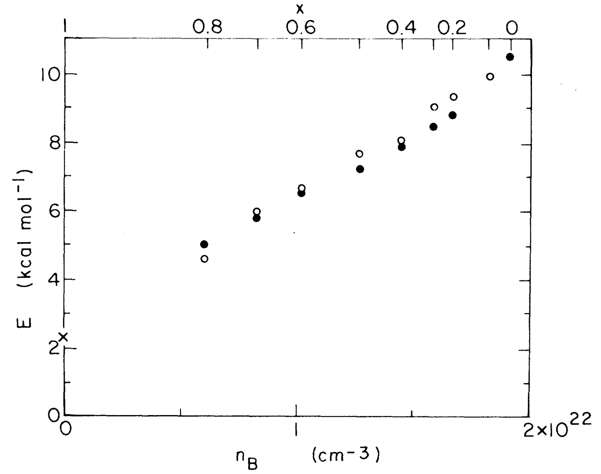

FIG. 1. Behavior of E_B (filled circles) and of the activation energies for conductivity E_A (empty circles) as a function of the density of the BO_4 units n_B. The cross indicates E_A for α-AgI (from Ref. 2). Notice that the activation energies are linear with n_B.

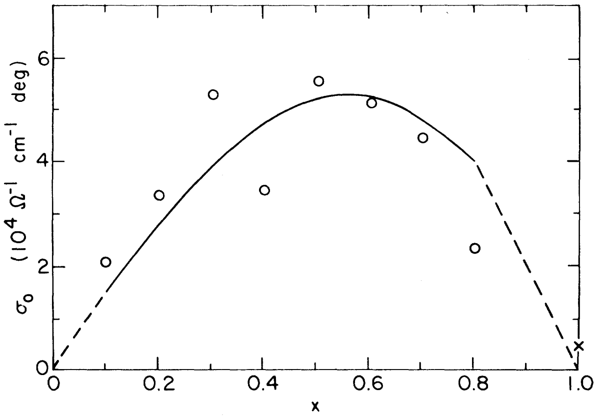

FIG. 2. The line gives the behavior of σ_0 calculated as explained in the text with $f=\frac{1}{6}$. Dashed portion extrapolates the theoretical behavior in the region where the density is unknown ($x<0.1$) and where the glass is not formed ($x>0.8$). The circles are the experimental values and the cross represents the prefactor of α-AgI (Ref. 2).

(a^+, b^+) and annihilation (a^-, b^-) operators promote the passage from ground to excited states and vice versa. The model Hamiltonian is

$$H=Aa^+a^- + \bar{B}b^+b^- + \tfrac{1}{2}C(a^+b^- + a^-b^+), \qquad (2)$$

where A is the energy needed to activate the ion diffusion in the absence of coupling with the disorder modes. It should have values of the order of the diffusional activation energies in ionic crystals. $\bar{B}$ has the meaning of "average" depth of the potential well which separates one configuration of the borate unit from another. We will then discuss when it is meaningful to replace the whole spectrum of the excitations of the glass with a single mode having energy of the interaction that couples the borate unit motion with the diffusion of the ion. Because of our definitions, the diffusion coefficient of the ion is proportional to the expectation value of the population operator

$$D \propto \langle a^+a^-\rangle_T, \qquad (3)$$

where the thermal average $\langle\,\rangle_T$ is taken over the four levels of the Hamiltonian of Eq. (1),

$$\begin{aligned} &E_0=0,\quad E_1=\tfrac{1}{2}\{A+\bar{B}-[(A-\bar{B})^2+C^2]^{1/2}\},\\ &E_2=\tfrac{1}{2}\{A+\bar{B}+[(A-\bar{B})^2+C^2]^{1/2}\},\quad E_3=A+\bar{B}. \end{aligned} \qquad (4)$$

We will assume that $A>\bar{B}$ and that the temperature is low enough that only the first excited level E_1 must be considered. Therefore

$$\langle a^+a^-\rangle_T = \sin^2(\tfrac{1}{2}\varphi)\exp(-E_1/RT), \qquad (5)$$

where $\varphi=\arctan[C/(A-\bar{B})]$. When $|C|>A-\bar{B}$ (strong coupling), we expect that every time the borate unit moves, one of the neighboring ions jumps. In this case, the diffusion coefficient may be written as

$$\begin{aligned} D&=\tfrac{1}{2}fP(x)l^2\omega_0\exp(-E_1/RT)\\ &=D_0\exp(-E_1/RT). \end{aligned} \qquad (6)$$

Here, f is the correlation factor,[8] l is the average jump distance, and $P(x)$ is the "average number" of borate units interacting with a mobile ion. $P(x)$ is expected to be dependent upon the history of the glass (quenching procedure, aging, etc.). With the Nernst-Einstein relation[9] the prefactor of the conductivity σ_0 can be expressed in terms of D_0 as

$$\sigma_0=e^2n_AD_0k^{-1}, \qquad (7)$$

where n_A is the AgI concentration. Figure 2 shows the calculated behavior of the prefactor σ_0 obtained by setting $l=3$ Å and $P(x)=4(1-x)$ since for $x=0.5$ there are twice as many BO_4 groups as AgI units and four seems an acceptable coordination number in a system where tetrahedral groups are certainly abundant. More significant than the agreement with the absolute values of the experimental conductivity prefactors seems to be the ability of the theory to predict a maximum of σ_0 vs x, even though its position depends on the form of $P(x)$.

Recent conductivity measurements[10] in some amorphous compounds of the system $(B_2O_3)_u$-$(Li_2O)_v(LiF)_y(Li_2SO_4)_z$ $(u+v+y+z=1)$ displayed a maximum of σ_0 as a function of the Li fraction $(2v+y+2z)$. These measurements qualitatively agree with the prediction of a model for conductivity by coupling with motions of the BO_4 groups. In fact, we assume that Li_2O has the predominant function of converting BO_3 rings into BO_4 tetrahedra and that, except for small $y+2z$ values, the experimental σ_0 is dominated by the contribution of the lithium ions bound to F^- and SO_4^{--}. By the coupling model, such a contribution depends on the number of BO_4 groups times the density of Li^+ not bound to oxygen. Therefore, $\sigma_0 \propto u'(y+2z)$, where u' is the smaller of either u of v and is half the molar fraction of BO_4. A similar reasoning can explain why ionic conductivity in $(B_2O_3)_u(Na_2O)_v(NaCl)_y$ $(u+v+y=1$ and $v<u)$[11] increases with the product vy.

Up to now, we have neglected the conductivity contribution of the M_2O groups (M is the monovalent cation) which provide the oxygen needed for the conversion of the BO_3 to the BO_4 units. Conductivities in the $(M_2O)_x(B_2O_3)_{1-x}$ systems[10,12] at the highest explored values of x (0.3–0.44) have activation energies close to 15 kcal mol^{-1} and, interestingly, again give estimates of attempt frequencies for M^+ diffusion in the range of the BO_4 vibrational frequencies. The need for very similar energies for oxide cation diffusion in the systems $(ML)_x(Ag_2O \cdot B_2O_3)_{1-x}$ (L is the anion) could be expected. If so, for the explored composition and temperature range,[2] the conductivity of the $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$ quenched compounds is essentially due to the silver of the AgI groups.

The suggestion that ionic conductivity is an opening to study disorder modes in ionic glasses is the most interesting implication of the coupling model. We believe that $\bar{B}$, and consequently E_1, are influenced by the possible collective nature of the borate unit motions. In effect, although $\bar{B}$ has the significance of interaction energy with a mean field, the participation of many borate units in the disorder mode should complicate the excitation spectrum of the BO_4 motions. At temperatures lower than explored ($\simeq 150$ K),[2] the details of the disorder-mode distribution may influence the conductivity. Low-lying excitations of glasses are expected to become predominant when the Boltzmann factor for the high-energy modes becomes negligible. Therefore, the Arrhenius behavior of conductivities should flatten at low temperatures in glasses. However, for the temperatures explored, a mean-field approximation is expected to be good since liquidlike aspects of the dynamics are predominant in glasses.[13]

From a technological point of view, a consequence of the coupling model is that conductivities can be almost independent of the ion diffusion energy [see Eq. (5)]. In effect, neither Ag^+ mobility nor ^{11}B NMR response is affected by replacement of iodine with bromine in $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$.[3] Replacement of chlorine with another halogen goes not change the conductivity of the B_2O_3-Li_2O-LiCl system.[11]

Concluding, we have shown that the coupling with a disorder mode is able to account for the conductivity prefactors of some BO_4-containing borate glass systems.

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