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ULTRASONIC STUDIES OF IONIC CONDUCTORS

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The role of ultrasonic techniques in the study of ionic conductors is reviewed. Attention is drawn to their non-Debye responses and the relationships of these to their electrical characteristics. Experimental studies of beta aluminas and silver ion conducting glasses are reviewed.

INTRODUCTION

In recent years ion conducting solids have been intensively studied throughout the world. The growth of interest in these materials was stimulated by the quest for alternative energy sources and in particular by the development of new advanced batteries such as the sodium sulphur battery. These batteries are able to store significantly more energy per kilogram than the familiar lead acid battery and are of great interest to advocates of electric vehicles. Unlike the lead acid battery, they employ a solid electrolyte to convey Na⁺ ions between the sodium and sulphur electrodes. The solid electrolyte is constructed of the Na⁺ ion conducting ceramic beta-alumina. Beta-alumina has a particularly high ionic conductivity and many other properties which are favourable to its utilisation in the sodium sulphur battery[1]. The interest in beta-alumina has encouraged research into a wide range of materials which exhibit high ionic conductivity.

The mechanism of ionic conduction in beta-alumina, and the vast majority of the other ionic conductors, is one of thermally activated ion hopping between atomic sites. Such ionic conductors are characterised by both: low activation energies and high densities of defects - vacancies or interstitial ions. Their ionic conductivities are thermally activated and determined by the products of their ion hopping rates and their mobile ion concentrations.

Ionic conductivity measurements alone do not provide a full characterisation of a conductor, because they provide no separate indication of the mobile ion concentration or the ion hopping rate. Thus an independent assessment of hopping rate, such as might be obtained using mechanical relaxation measurements, has great potential value. These solid electrolytes' very low activation energies result in hopping rates which may be as high as several GHz at room temperature; in sharp contrast to the very much lower atomic hopping frequencies familiar to those involved in internal friction studies of atomic diffusion in solids. Consequently, ultrasonic attenuation measurements (at MHz frequencies) are the preferred means of studying mechanical relaxation effects in these ionic conductors.
The purpose of this review is to outline the progress that has been made in the study of solid electrolytes by, principally, ultrasonic techniques. Particular attention will be drawn to the correlation between the mechanical responses observed and those obtained independently in a.c. electrical studies. The review will not attempt to encompass the glassy two-level system effects which have been studied ultrasonically at very low temperatures[2].

**IONIC CONDUCTIVITY**

The conductivities, $\sigma$, of the majority of ionic conductors vary with temperature, $T$, as

$$\sigma = \sigma_0 / T \exp(-E/kT) \quad (1)$$

where $E$ is an activation energy, $k$ is Boltzmann's constant and the conductivity prefactor $\sigma_0$ is given by the expression

$$\sigma_0 = N e^2 a^2 \gamma k^{-1} \exp(S/k) \omega_0 \quad (2)$$

where $c$ is the concentration of mobile ions distributed over $N$ equivalent sites per unit volume, $a$ is the hopping distance, $e$ the electronic charge, $\gamma$ is a correlation factor, $S$ is the entropy of activation and, $\omega_0$, is the ion vibrational frequency. The ion hopping frequency, $\omega_p$, which might be obtained experimentally is given by

$$\omega_p = \omega_0 \exp(S/k) \exp(-E/kT) = \omega_e \exp(-E/kT) \quad (3)$$

where $\omega_e$ may be regarded as being an effective attempt frequency, incorporating the entropy term.

**ULTRASONIC ATTENUATION IN IONIC CONDUCTORS**

In solid electrolyte materials, experimental attenuation studies give peaks that are much broader than an ideal Debye peak, (see below). Different approaches have been used to characterise such non Debye-like peaks. The traditional approach, especially in electrical relaxation studies, is to treat them as the sum of a number of Debye-like peaks, corresponding to a range of relaxation times arising from a distribution of activation energies, $E$. The attenuation $\alpha$, at angular frequency $\omega$ then takes the form [3]:

$$\alpha = \Delta \int \frac{g(E)\omega^2\tau(E)}{1 + \omega^2\tau^2(E)} dE \quad (4)$$

where the distribution function, $g(E)$, may be obtained from the shape of the relaxation peak. This approach depends on the assumption that ion migration may be treated in terms of a set of non-interacting, Debye-like, processes. In solid electrolytes, however, mobile ion concentrations are large and conduction mechanisms are thought to be co-operative.

The parameter, $\Delta$, the relaxation strength, determines the magnitude of the attenuation peak. It is related to the strain dependence of the mobile ion site energy, or deformation potential, $B$, by [3]:

$$\Delta = \frac{N e B^2}{4 \pi \rho v^3 kT} \quad (5)$$

in which $N$ is the number of mobile ions, $v$ is the velocity of the sound wave, $\rho$, is the density of the solid, $T$ is absolute temperature and $k$ is the Boltzmann constant. The direct relationship between the magnitude
of the attenuation and the number of mobile ions contributing, \( N \), is to be expected. In addition, the attenuation is inversely proportional to the cube of the sound velocity, \( v \).

The validity of the distribution of relaxation times, or activation energies, approach has been questioned by Jonscher. He has shown [4] that the relaxation phenomena observed in a wide variety of materials exhibit a power-law type of frequency dependence, often spanning many decades of frequency, and suggests that there is no reasonable justification for attributing such extensive effects to distributions of relaxation times. Jonscher demonstrated that dielectric loss peaks conform to a "universal" response function, which was subsequently shown to be attributable to many-body processes by Dissado and Hill [5]. The author suggested [6] that the same response function could be used to account for the attenuation peaks obtained in ionic conductors, ie that ultrasonic attenuation peaks take the form:

\[
\alpha \propto (1/T)[(\omega / \omega_p)^{-m} + (\omega / \omega_p)^{1-n}]^{-1}
\]

(6)

where \( m \) and \( n \) are power-law exponents, which take values between 0 and 1, and \( \omega_p \) is a characteristic, thermally activated frequency associated with the attenuation peak and suggested to be [6] the ion hopping frequency. Eqn. 6 reduces to the equation for a single Debye-like process when \( m=1, n=0 \) and \( \omega_p = \tau^{-1} \). The value of the ratio \( \omega / \omega_p \) at the attenuation peak depends on the values of \( m \) and \( n \) and is given by the condition:

\[
\frac{\omega}{\omega_p} = \left[ \frac{m}{1-n} \right]^{1/(1-n+m)}
\]

(7)

Recently, Dyre [7,8] has demonstrated that power-law responses can be produced by a simple exponential distribution of relaxation times and Palmer et al [9] have suggested that in strongly interacting glassy materials the power-law, or Kohlrausch, forms of relaxation emerge naturally.

RELATIONSHIP BETWEEN ULTRASONIC AND ELECTRICAL RESPONSES

Electrical measurements of ionic conductors are conventionally made across the frequency range 100 Hz to 10 MHz at fixed temperatures. It is widely recognised that such measurements exhibit non-Debye-like power law increases with frequency. Hence it is natural to look for a relationship between ultrasonic and electrical characteristics. The frequency dependence of the bulk conductivity of an ionic conductor may be described by [10]

\[
\sigma (\omega) = K \omega_p^{1-n_1} \omega^{n_1} + K \omega_p^{1-n_2} \omega^{n_2}
\]

(8)

in which \( n_1 \) and \( n_2 \) are power law exponents <1 and \( K \) is a combination of a number of terms, including mobile ion concentration, \( N \). In practice the low frequency exponent, \( n_1 \), is often very small and at low frequencies the conductivity is approximately constant; taking a value equal to the true d.c. ionic conductivity.
The above expression has been obtained [11] by an analysis of ionic conductivity involving many-body interactions amongst the ions. In that analysis, the two terms in eqn. 8 have the same origin as those in eqn. 6 which describe ultrasonic attenuation. The simplicity of the two expressions facilitates a particularly straightforward parameterisation of both conductivity and ultrasonic data. Thus the two characteristic frequencies, \( \omega_p \), may be compared as may the power law exponents, \( n, m, n_1, n_2 \).

**REVIEW OF ULTRASONIC STUDIES OF SOLID IONIC CONDUCTORS**

**Single Crystal Beta-alumina**

![Graph showing attenuation vs temperature for ultrasonic waves in beta-alumina.](image)

Fig.1. Measurements of the attenuation of longitudinal waves propagated along the c-axis direction in a single crystal of beta alumina.

Measurements of the attenuation of longitudinal ultrasonic waves propagating in the same direction as the conduction plane in a single crystal of beta-alumina showed a single broad peak which was displaced to higher temperatures with increasing frequency [12], fig. 1. Such beta-alumina ultrasonic data were found to accurately fit the Jonscher expression, eqn. 6, as shown in fig.2, [13]. The best fit to the data was obtained for power law exponents \( m \) and \( n \) of 1 and 0.65, respectively.

The values of the characteristic frequency, \( \omega_p \), obtained using the peak condition, eqn.7, are shown plotted in Arrhenius format in fig.3. These data are seen to be in very good agreement with lower frequency internal friction data [14-16] obtained at much lower temperatures. The
Debye Theory
Inverse Temperature \( \frac{1000}{T} \) (K\(^{-1}\))

Fig. 2. Measurements of the attenuation of longitudinal waves propagated along the c-axis direction in a single crystal of beta-alumina plotted against inverse temperature. The solid line through the data is a fit of eqn. 6 using the parameters shown in the figure.

Activation energy obtained from the combined ultrasonic and internal friction data is in excellent agreement with the value, 0.16 eV, established by ionic conductivity measurements. In addition, the attempt frequency is close to the value 2 \( \times 10^{12} \) Hz, obtained from infrared absorption [17]. Hence there is good reason to believe that the mechanical relaxation peaks can be attributed to sodium ion hopping in beta-alumina and that the technique might be of value for determining hopping rates in other ionic conductors.

Electrical conductivity data, obtained from a similar single crystal sample of beta-alumina were analysed using eqn. 8 [10]. The values of the exponent \( n_2 \) were close to zero (0.035) and for \( n_2 \) were 0.6 above 120K but increased somewhat at lower temperatures. There is a remarkable similarity in the values of the mechanical exponent \( n \) and the electrical exponent \( n_2 \). Both correspond the high frequency parts of the respective responses, indicating a common origin. The values of the low frequency mechanical exponent \( m \) and the electrical exponent \( n_1 \) are both close to the Debye-like values, 1 and 0, again indicating a common origin. Values of \( \omega_0 \) obtained from the conductivity data are also shown in fig. 3. The close agreement with the ultrasonic and internal friction values indicates that the relaxation times for the electrical and mechanical phenomena are very similar. This agreement added considerably to the contention that a.c. electrical measurements could be used to obtain ion hopping rates. Simmons et al [15] have proposed a microscopic model to explain the
Fig. 3. An Arrhenius plot of the characteristic hopping frequencies obtained in the analysis of ultrasonic attenuation, internal friction and a.c. electrical data of a single crystal of beta alumina.

Mechanical relaxation and electrical conduction in beta alumina. They attribute the observed anelastic relaxation to the established location of the sodium ions on crystallographically inequivalent sites. In addition, they showed that electrical and mechanical relaxation times should differ by a factor of only about two. The precision of the experimental data is insufficient to confirm this prediction.
Polycrystalline $\beta/\beta''$-aluminas.

Fig. 4. (a) Measurements of the attenuation of longitudinal waves in a polycrystalline sample of 70% $\beta''$, 30% $\beta$-alumina. (b) Measurements of the attenuation of longitudinal waves in a polycrystalline sample of >90% $\beta''$, <10% $\beta$-alumina.
Beta-alumina can be produced in a meta-stable $\beta^*$ phase which has been extensively investigated because of its higher ionic conductivity. Large single crystal samples have not been available for ultrasonic work. However, commercially produced polycrystalline material containing a substantial proportion of the $\beta^*$ phase, of the type used for sodium sulphur battery electrolytes, has been studied. Measurements of the attenuation in a polycrystalline sample of composition 70% $\beta^*$, 30% $\beta$ alumina [18] are shown in fig. 4a. These data have been treated in the same way as the single crystal data. An activation energy of 0.14eV and an attempt frequency of $3 \times 10^{12}$ Hz were obtained, with $m=1$ and $n=0.67$ [19]. These values are remarkably similar to the single crystal beta-alumina values, despite this being the minority phase in this polycrystalline sample. Similar measurements on an almost pure $\beta^*$ alumina (of composition $\beta^*$=90%, 10% $\beta$), fig. 4b, showed no evidence of an attenuation peak in the temperature range in which they were found in the lower $\beta^*$ content sample, fig. 4a. All that was found was a steady increase in attenuation at high temperatures. This absence of the low temperature peak indicates that anelastic relaxation does not occur in the $\beta^*$ phase and further supports the conclusion that the attenuation peaks in Fig. 4a are solely due to the $\beta$ content of the 70% $\beta^*$, 30% $\beta$ sample. In $\beta^*$-alumina, the mobile sodium ions occupy crystallographically equivalent sites and since the equivalency of these is unaffected by an applied stress, anelastic phenomena are not expected to occur.

Recently, Patel and Nicholson [20] have reported ultrasonic studies of a range of polycrystalline $\beta/\beta^*$-aluminas containing one or a mixture of two alkali ions (Na, K). Their results for the single ion samples are similar to those for the 70% $\beta^*$, 30% $\beta$, discussed above. However, an additional attenuation peak was found at temperatures above 400K which was attributed to ion interactions in the grain boundaries. The data for the mixed-alkali, Na/K, showed four attenuation peaks in two pairs at high and low temperatures. It was suggested that this showed that the activation energy of the Na$^+$ ions had been modified by the presence of the K$^+$ ions- the mixed alkali effect. In complex systems such as these, ultrasonic techniques exhibit a range of effects which deserve a thorough investigation.

Silver Ion Conducting Glasses

The AgI-Ag oxysalt glasses are a family of Ag$^+$ ion conducting solids with room temperature ionic conductivities comparable to that of beta alumina. Measurements of the attenuation of longitudinal waves in a sample of $3\text{AgI}_2\text{Ag}_2\text{MoO}_4$ [21] are shown in fig. 5. The attenuation peaks are in many respects similar to those found in the beta aluminas. Like those in the beta aluminas, they are considerably broader than a Debye peak and they appear to be thermally activated. However, the magnitudes of the attenuation peaks in the ion conducting glasses are much greater than in the beta aluminas. The amplitude of the 1.25 MHz peak is similar to that found at 70 MHz in the polycrystalline $\beta/\beta^*$ sample and to that found at 200 MHz in the single crystal of beta alumina. The 10 MHz data, fig. 5, are incomplete because of the magnitude of the attenuation at the peak. It would be wrong to jump to the conclusion that the coupling between the ultrasonic wave and the ions is much greater in the glasses. The peak magnitude depends on a number of other factors, eqn. 5, and particular account should be taken of its dependence on the velocity of sound, $v$. The sound velocities of the beta aluminas and the glass are shown in Table 1. The very low sound velocity in the glass, through eqn. 5, produces the substantial enhancement of attenuation phenomena whilst the rather high sound velocities of the beta aluminas reduce them. Analysis of the peak amplitudes, using estimates for mobile ion concentration, N , from conductivity studies [24], reveals deformation potentials, B, of comparable magnitude.
Fig. 5. Measurements of the attenuation of longitudinal waves in 3AgI.Ag2 MoO4 glass. The solid line through the 1.25 MHz data is a fit of eqn.6, as explained in the text.

The curve fitted to the 1.25 MHz peak, fig. 5, was obtained using eqn.6 with m=0.8 and n=0.7 and assuming an activation energy of 0.27 eV [21]. The exponent n is identical to the value of n2 used in eqn.8 to fit the frequency dependence of the a.c. conductivity [21]. In addition, estimates of mechanical and electrical relaxation frequency, ωo, were found to be in close agreement. As in beta alumina, this evidence strongly suggests that ultrasonic and electrical techniques probe the same basic ion hopping process in this glass.

Carini et al [23,24] have presented a series of extensive ultrasonic studies of AgI-Ag borate ion conducting glasses. Several groups of glasses, with either variable AgI content and/or variable Ag2 O.B2O3 ratio were studied. All the glasses showed a single, broad, thermally activated attenuation peak of amplitude comparable to that found in the AgI-Ag molybdate glass discussed above. The activation energies indicated were similar to those obtained from electrical conductivity measurements. The broad attenuation peaks were fitted well by eqn.4 using a distribution of relaxation times obtained from a Gaussian distribution of barrier heights. They estimated the deformation potential, B, making the assumption that all the Ag+ ions present contributed to the relaxation loss and obtained a value of 0.33 eV; which is comparable to the values for the beta aluminas and the AgI-Ag molybdate glass, Table 1.
Table 1. Values of deformation potentials, B, obtained from equation 5 using densities, \( \rho \), and sound velocities, \( v \), shown, carrier concentrations, \( N \), from [22] and the ultrasonic attenuation peaks in the appropriate figure.

### CONCLUSIONS

The comparatively small number of ultrasonic attenuation studies of ionic conductors have amply demonstrated the potential of the technique. The phenomena observed have been found to be closely related to the mechanics of the ionic conduction process. It appears to provide a technique for estimating ion hopping rate and, when combined with conductivity studies, of determining mobile ion concentrations. The discovery of the close relationship of the mechanical and electrical responses has added significantly to the development of the understanding of a.c. conductivity and the acceptance of hopping rates obtained by a.c. analysis.

The appearance of a technique for the determination of ion hopping rates in solid electrolytes has drawn attention to the formerly neglected entropy of activation term, eqn.3. In many cases [22] effective attempt frequencies two or more orders of magnitude larger than the lattice vibrational frequency have been found. This enhancement, which may be attributed to the entropic term in eqn.3, plays a considerable part in determining the magnitude of the ionic conductivity. Prior to this work the significance of this term in providing the useful conductivity of many solid electrolytes had not been appreciated.

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