Coupled fast and slow relaxation dynamics in ion conduction g solids

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Received 10 January 2013; revised 20 February 2013; accepted 14 March 2013

The observations of slow relaxation process within a wide range of timescales larger than microscopic vibrational times are well established in the motion of charged defects in ionic and electronic solids. A complex relaxation time function \( \phi(t) = \exp[-(it)^{\beta}] \) is proposed, where \( \Gamma(t) = (it)^{\beta} \), the relaxation time \( t \) (referred as fast relaxation time) and \( \Gamma \) delays the fast relaxation time \( t \) to \( t^{\beta} \) (referred as slow relaxation time), \( \beta > 0 \) and \( \beta < 1 \). The \( \beta \) is playing a key role and it couples fast and slow relaxation dynamics processes. The physical picture for the \( \beta \) is envisioned in terms of trapping and correlation of mobile hopping charge polarization in the disordered host lattice. Ac conductivity in ion conducting solids is interpreted by considering fast and slow scales of relaxation dynamics of charge carriers.

Keywords: Ion dynamics, Slow and fast relaxation processes, Ac conductivity, Complex impedance data analysis

1 Introduction

The understanding of relaxation mechanism and charged particles’ dynamics through the solids is of fundamental importance and it is a subject of great interest to physicists, chemists and materials scientists. The observations of slow relaxation process within a wide range of timescales larger than microscopic vibrational times are well established to study the motion of charged defects in ionic and electronic solids. The slow relaxation process is known as non-Debye relaxation or anomalous relaxation in ion conducting solids\(^1,2\). The slow relaxation process manifests in numerous dynamical probes, like ac conductivity, dielectric relaxation, mechanical relaxation, nuclear spin-relaxation etc. Dieterich\(^3\) predicted that the improvement in understanding the non-Debye relaxation or slow relaxation is not possible as long as the empirical and phenomenological laws cannot be justified further\(^1,2\).

The empirical and phenomenological function in the time domain are: (i) stretched exponential relaxation function \( \phi(t) = \exp[-(it)^{\beta}] \), where \( \beta \) is Williams-Watts exponent \( 0 < \beta < 1 \); (ii) Jonscher’s power law \( \phi(\omega) \propto \omega^{\beta} \), and its corresponding dielectric loss is \( \varepsilon''(\omega) \propto \omega^{\beta-1} \).

Kohlrausch-Williams-Watts\(^3\), Jonscher’s power law\(^4,5\), Havirliak-Nigami\(^6\), Cole-Cole\(^7\), Cole-Davidson functions\(^8\), coupling model of Ngai\(^9,10\), Funke et al\(^11\), concept of mismatch and relaxation, macroscopic and microscopic models of Dyre\(^12,13\) and corrected model of Macdonald\(^14\) are describing the experimental features of ac conductivity. However, the transparent interpretation of ac conductivity and the quantification of correlated non-random hopping are still appearing to be difficult. Also, it was not possible to establish the dependence of the exponents in (i)-(vi) on the physical characteristics of solids, for example, depolarization current, hopping frequency and temperature. In addition to this, the concept of slow relaxation and the non-random bounce-back mechanism, coupling, and correlation are not clear in terms of hopping and polarization process.

In the present paper, a complex relaxation function for the hopping charge carrier polarization is presented for the ion conducting solids and explained physical basics for the important universal features of ac conduction. The fast (random or uncorrelated) relaxation process and the slow (non-random or correlated) relaxation processes are shown to be responsible for important features of ac conduction. The physical basics for fast and slow relaxation time
processes are explained in terms mobile hopping charge carrier polarization and their corresponding barrier energy.

2 Complex Relaxation Function

In our earlier work\textsuperscript{15,16}, an unusual anomalous relaxation function is identified by modifying empirical form of Cole-Cole complex permittivity as:

\[ \varepsilon^*(\omega) \approx 1/[1+(i\tau)g_{\phi}^{-\alpha}] \]  \hfill (1)

where \(0<\alpha<1\) is exponent, \(\tau\) is relaxation time and it is thermally activated, \(\omega\) is the applied frequency. Integrating the inverse Laplace transform of Eq. (1) provides a complex relaxation function:

\[ \phi^*(t)=\exp[-(t/\tau)^{g_{\phi}^{\alpha}}] \]  \hfill (2)

For Cole-Cole function, it is not possible to obtain the corresponding time domain relaxation function by integrating the inverse Laplace transform. However, the exponent \(\alpha\) is used to account for anomalous dispersion in frequency domain either in terms of distribution of relaxation time or energy storage and dissipation in terms of circuit elements like resistor and capacitor.

The role of phase \(i^{\pm\sigma}\) and physical significance of exponent \(g\) in Eqs (1 and 2) have been investigated. We have assumed, under thermo-dynamical condition, the mobile ions and oppositely charged disordered host lattice resemble an assembly of dipoles and relax like a dipolar relaxation. The charges involved in the depolarization processes are identified in the disordered solids. Initially, the ionic charge carrier density. Since mobile ions are actively involved in the charged disordered host lattice, at the subsequent level, under the same thermo-dynamical condition, a fraction charge, \((1-g)q_{nc}\) is trapped in certain sites of disordered host lattice and remaining charge carriers \(gq_{nc}\) are involved in the depolarization process. The polarization rates of the charges, \(q_{nc}\), \(gq_{nc}\), and \((1-g)q_{nc}\) are coupled and correlated in terms of g. The depolarization process of charges \((1-g)q_{nc}\) and \(gq_{nc}\) are sort of a non-random correlated and slower relaxation processes.

To extract both fast and slow relaxation dynamic processes, Eqs (1 and 2) are rewritten after little algebra as:

\[ \varepsilon^*(\omega) \approx [1+i\omega/T^*]^{-1}[1+i\omega\Gamma^*]^{-1} \]  \hfill (3)

\[ \phi^*(t) \exp[-(t/\tau)^{\Gamma^*}] \exp(-t/\tau) \]  \hfill (4)

\[ \Gamma^*=(\nu/\tau)^{\sigma}, \]  \hfill (5)

\[ \tau^*=1/\omega_p^* \tau \Gamma^* \]  \hfill (6)

\([\nu]=(\text{Hz})^{\pm\sigma}\) is a dimensional factor\textsuperscript{17} and for the convenience it is omitted further, and \(\nu=\sqrt{-1}\). When the exponent \(g=1\), we have an usual exponential relaxation function \(\phi(t)=\exp(-t/\tau)\) and its corresponding complex permittivity \(\varepsilon^*(\omega) \approx 1/(1+i\omega\tau)\). In Eqs (3 and 4), we find three time scales of thermally activated hopping frequencies and these are given by:

(i) the fast hopping frequency \((g=1)\):

\[ \omega_0=1/\tau_{0}=\omega_0 \exp(-E_0/k_0T) \]  \hfill (7)

where \(E_0\) is the activation barrier energy for hopping with attempt frequency \(\omega_0\);

(ii) the time delay factor \((0<g<1)\):

\[ \omega_0^{-1}=|\gamma|=1/|\Gamma|=1/\tau_{\pm}=\omega_0^{-1}\exp(-E_0/k_0T) \]  \hfill (8)

\[ \gamma=\omega_0^{-1}\exp(-E_0/k_0T) \cos[E_1/k_0T]/(1-\text{tan}[E_1/k_0T]) \]  \hfill (9)

with an activation barrier energy \(E_b=(1-g)E_{th}\) which is a reduction in barrier energy \(E_{th}\) \(E_{th}=(\pi/2)(1-g)k_0T\) is a lattice heat bath energy;

(iii) the slow hopping frequency \((0<g<1)\):

\[ \omega_p^*=|\omega|=1/\tau_{\pm}=\omega_0\delta \exp(-E_c/k_0T) \]  \hfill (10)

\[ \omega_p^*=\omega_0\exp(-E_c/k_0T) \cos[E_1/k_0T] \]  \hfill (11)

with an activation energy barrier \(E_c=gE_{th}\) which is equal to the change in energy barrier height \(E_{th}\). Further, \(\omega_p^*\) and \(\tau_\pm\) can be written as:

\[ \omega_p^*=(\omega_0+\omega_0)_{+} \]  \hfill (12)

\[ \omega_0=\omega_0\cos[(1-g)\pi/2]; \omega_0=\omega_0\sin[(1-g)\pi/2] \]  \hfill (13)

\[ \tau_G=\tau^* \cos[(1-g)\pi/2]; \tau_G=\tau^* \sin[(1-g)\pi/2] \]  \hfill (14)

with the condition \(\omega_p^*\tau^*=1, \omega_p^*\tau^*=1\). Schematic features of potential energy barrier for these fast and slow relaxation processes are shown in Fig. 1
3 Barrier Energy for Fast and Slow Relaxation Processes

Figure 1 shows the schematic features of barrier energy for the hopping ion for the processes $g=1$ and $0<g<1$. For $g=1$ (black curve), the charge involved in the hopping process is $q$ with barrier energy $E_B$. At certain host lattice sites, the part of the hopping charge carriers $n_i(1-g)q$ are trapped due to disorder and hence, the charge density involved in the hopping process becomes $n_iq$, where $n_i$ is the carrier density. Effective lattice charge $gq$ and $(1-g)q$ and their interaction leads to change in the barrier energy. For $0<g<1$ (dotted red curve), the effective charge involved in the hopping at the lattice site is $gq$ with barrier energy $E_c=gE_B$. For $0<g<1$, the ions that are jumping towards A→B and B→A, the potential barrier energy $gE_B$ becomes $gE_B\xi(gq)b/2$, and $gE_B+(\xi(gq)b)/2$, respectively, where, $\xi(gq)b/2$, shift in energy level due to the external field $\xi$, and $b$ is the hopping distance. Consider an ion performing a successful hop from A to B in a time interval $0<t<\tau$. In a first step, it has to surmount the energy barrier, $E_B$, between these sites of distance $a$, with highest activation energy, $E_B$, for the hopping. Because of the mobile ion trapping, clustering and repulsive interaction, the ions tend to stay more than the $\tau$. If the ion hops in a neighbouring site, the repulsive interactions cause a change in the potential barrier as shown in the dotted line in Fig. 1. After the fast hopping, i.e., $\tau<\tau<\infty$, the neighbouring mobile ions rearrange in the course of their own motion and become slow in the relaxation of B. Thus, this process changes the fast process potential barrier $E_B$, by a factor of $g$, and effective potential barrier height for the slow process becomes $E_c=gE_B$.

For effective charge, $gq$, jumping towards A→B and B→A, the net transition probability for hopping A to B, is given by Eqs (7) and (10), for $g=1$, and for $0<g<1$, respectively with condition $\xi(gq)b<<k_B T$, where $E_B$ activation energy for $g=1$ with fast hopping frequency $\omega_p$, and $E_c=gE_B$ activation energy for slow relaxation process for $0<g<1$ with hopping frequency $\omega_h$. The lattice heat bath for the hopping process is $E_{L}=(\pi/2)(1-g)k_B T$ and it is feedback energy through the phase memory delay process in $\phi'(t)$. This implies, the barrier energy $E_B$ with lattice heat bath energy $E_L$, leads to slow relaxation rate $\omega_h$, with correlation rates $\omega_p$, and $\omega_h$. The dc conductivity $\sigma(0)$, is defined at fast hopping frequency $\omega=\omega_p$, and it is given by:

$$\sigma(0)=\sigma(\omega_p)=(n_i(qa)^2\omega_p/\xi k_B T)$$

$$=(N_i(qa)^2/\xi k_B T)\omega_p \exp(-E_B/k_B T) \quad \text{(15)}$$

where $q$ is the ionic charge, $\xi$ is the geometric factor, $n_i=N_i \exp(-E_B/k_B T)$. $E_B$ is the energy for dissociation of defects, $E_0=E_p+E_B$, is the activation energy for the dc conductivity. The ac conductivity is defined at $\omega=\omega_c$ (cross-over frequency or slow hopping frequency) and it is given by:

$$\sigma(\omega_c^*)=(n_i(qa)^2\omega_c^*/\xi k_B T)$$

$$=(N_i(qa)^2\omega_c^*/\xi k_B T)\exp(-E_{acc}/k_B T) \quad \text{(16)}$$

where $E_{acc}=E_p+gE_B$, is the activation energy for slow hopping conductivity. The number of charge carriers in the slow hopping conductivity is $n_iq$. The magnitude of $\sigma(\omega_c^*)$, is obtained from the imaginary part of complex resistivity, $\rho(\omega)$, and it is given by:

$$\sigma(\omega_c^*)=\sigma(\omega_p)/[\tan(\pi/4)] \quad \text{(17)}$$

The $\sigma(\omega_c^*)$ is responsible for the dispersion in the ac conductivity and permittivity loss.

4 Salient Features of the Complex Relaxation Function

The time development of $\phi(t)$ is explained for fast and slow relaxation for a typical values of $\tau=10^{-9}$s and $g=0.2$, and the results are shown in Fig. 2(a-b). For $\tau=10^{-9}$s, the delay factor is $(1/\tau)^{1/2}=501.19$, for $g=0.7$, and therefore, $\tau^{1/2}=5.012\times10^{7}s$. The correlation rates and times are: $\omega_p=9.06\times10^{7}$rads/s $\omega_h=1.78\times10^{9}$rads/s, $\tau_p=2.28\times10^{7}$s and $\tau_h=4.47\times10^{7}$s. The mobile charge contributions and their interactions, thermally driven local fluctuation are responsible for current-current fluctuation and correlation. The equilibrium current-current fluctuation slows down the relaxation time $\tau$. 

![Fig. 1 — Schematic picture showing potential barrier energy for $g=1$ (black) and for $0<g<1$ (red dots) with hopping distances $a$ and $b$.](image-url)
by a factor of $(1/\tau^g)^g$, and hence the slow relaxation time $\tau^g$. The slow relaxation and the time development of current-current fluctuation and correlation are evident in

$$J'(t) = -d\phi(t)/dt; \quad J''(t) = \cosh[t(\omega_k); J(t) = \exp[-t\sigma_k]\sin[\tau_k]$$  \hspace{1cm} (18)

$$J'(t) = \exp[-t\omega_k]\cosh[t(\omega_k); J'(t) = \exp[-t\omega_k]\sin[\tau_k]$$  \hspace{1cm} (19)

The $J'(t)$, $J''(t)$, and $J(t)$ contain the random hopping frequency $\omega_k$, and non-random hopping frequency $\omega_p^g$ and the correlation frequencies $\omega_k$ and $\omega_p^g$.

The hopping frequency $\omega_p^g$ is a dynamically evolved quantity. For $t/\tau^g > 1$, the functions $J'(t)$, $J''(t)$, and $J(t)$ have the tendency to fluctuate with frequency, $\omega_k$, for $t/\tau^g \ll 1$. These are thermally driven local fluctuations of space charge decay. The response current, $\omega(t)$, is negligible for $t/\tau^g > 1$, and it is hardly seen in the closed region in Fig. 2(a). Although, the response current $\omega(t)$ is insignificant for $t/\tau^g > 1$, the process slows down $\tau$ by a factor of $(1/\tau)^g$. However, around $t=\tau^g$, $\tau_R$, $1/\omega_k$, and $1/\omega_p^g$, the $\omega(t)$ is significant. This is an interesting feature of the proposed function $\phi(t)$ and it is explicitly shown in Fig. 2(b) by plotting the real and imaginary parts of natural logarithm of $\phi(t)$:

$$(\ln[\phi(t)])' = -(\tau \omega_k) \quad \text{and} \quad (\ln[\phi(t)])'' = -\tan^{-1} \tan(\tau \omega_k)$$  \hspace{1cm} (20)

Fig. 2 — (a) Typical behaviour of $\phi'(t)=\exp[-(-\tau^g \ln^g)]$, for $t=10^5$ s, $g=1$, $g=0.7$ as a function of $\phi(t)$. (b) The $\ln[\phi'(t)]=-(\tau \omega_k)$ and $\ln[\phi'(t)]=-(\tau \omega_k)$ as a function of the $\ln[\phi'(t)]$. The symbols are positions of correlation times $\tau^g$ and $\tau$ as a function of $\log(t)$. The symbols in Fig. 2(a-b) show the magnitudes of respective quantities evaluated with corresponding functions at the allowed relaxation and correlation times $t=1/\omega_p$, $1/\omega_k$, $1/\omega_k$, and $1/\tau_R$ and $\tau_k$. All these time scales are thermally driven local fluctuations of coupled and correlated mobile hopping charge carriers $qn_c$, $gqnc$ and $(1-g)qn$. The mobile charge correlation is the signature of slow relaxation process, and it is clearly seen in the present function in a coupled manner with slow and fast process.

5 Complex Relaxations in ac Conductivity and Resistivity

Complex conductivity, resistivity and permittivity for the resistance-capacitance parallel combination with complex relaxation time are given by:

$$\sigma^+(\omega) = 1/\rho^+(\omega) = \sigma(0)(1+i\omega \tau^g)$$  \hspace{1cm} (21)

$$\epsilon^+(\omega) = \sigma^+(\omega)/(i\omega \epsilon_0) = \sigma(0)(1+i\omega \tau^g)/(i\omega \epsilon_0)$$  \hspace{1cm} (22)

The real and imaginary parts of complex conductivity, resistivity and permittivity are found to be:

$$\sigma'(\omega) = \sigma(0)(1+\omega \tau_R); \quad \sigma''(\omega) = \sigma(0)\omega \tau_R$$  \hspace{1cm} (23)

$$\rho'(\omega) = \rho(0)(1+\omega \tau_i)[1+2i\omega \tau_i(\omega \tau_R)^2]; \quad \rho''(\omega) = \rho(0)\omega \tau_R[1+2i\omega \tau_i(\omega \tau_R)^2]$$  \hspace{1cm} (24)

$$\epsilon'(\omega) = \sigma(0)\tau_R/\epsilon_0; \quad \epsilon''(\omega) = \sigma(0)(1+\omega \tau_i)/(i\omega \epsilon_0)$$  \hspace{1cm} (25)

where $\tau_R$ and $\tau_i$ are given by Eq. (12). In Eqs (21-25), $g=1$ is the fast hopping process, and $0<g<1$, the slow non-random and correlated hopping process. From Eq. (24), when $g=1$, at $\omega=\omega_p$, $\rho(\omega_p)=\rho(0)/2$, for $0<g<1$, at $\omega=\omega_p$: $\rho''(\omega_p) = (\rho(0)/2) \tan(\pi g/4)$  \hspace{1cm} (26)

Present model provides better physical insight for the ac conductivity in terms of fast and slow hopping processes having coupling and correlation.

Figure 3(a) shows a plot of $\rho'(\omega)$ as a function of $\log(\omega)$ for $\omega_p=1/\tau(t)=10^9$ rad/s for $g=0.7$. The corresponding time domain depolarization and relaxation are shown in Fig. 2(a-b). The exponent $g=1$ is the fast process and $g=0.7$ is the slow process. The increase in full width at half maximum of $\rho'(\omega)$ is an indication of slow relaxation. The slow process peak in the imaginary part of complex resistivity $\rho'(\omega)$ is
found at \( \omega = \Omega _p \) and it is the slow relaxation rate. In slow relaxation process \((0<\omega<1)\), the full width at half-maximum of \( \rho _0(\omega) \) is increased. The full width at half-maximum of \( \rho _0(\omega) \) is found to be:

\[
\Delta \omega = 2 \log [h + (h^2 - 1)^{1/2}]
\]

where \( h = 2 + \sin[(1-g)\pi/2] \) and its magnitude is shown in Fig. 3(a) for \( g = 0.7 \). The symbols on the curves in Fig. 3(a) refer the respective quantities evaluated with corresponding functions at \( \omega = \omega _p , \omega _k , 1/\tau _R \) and \( 1/\tau _I \).

The parametric equation of \( \rho _0(\omega) \) is obtained by eliminating \( \omega \) and \( \tau _{p} \) and it is found to be:

\[
\{(-\rho _0''+(\rho _0'')^2+(\rho _0''')^2)\cos[(1-g)\pi/2]
+ (\rho _0'')\sin[(1-g)\pi/2]\}\cos[(1-g)\pi/2]=0 \quad \ldots \ (28)
\]

The parametric Eq. (28) is a function of exponent \( g \). Fig. 3(b) shows the parametric plot of Eq. (28). The semi-circle is found for \( g = 1 \), and depressed semi-circle for \( 0<\omega<1 \), and it is the characteristics feature of the slow relaxation. The symbols on the curves refer the respective quantities evaluated with corresponding functions at \( \omega = \omega _p , \omega _k , 1/\tau _R \) and \( 1/\tau _I \).

6 Ac Conductivity Data Analysis and Extraction of Physical Parameters

As a first step, the proposed model has been used to analyze the ac conductivity data of single crystal of NaCl: (doped with 50 ppm Zn\({ }^{2+}\)) in the temperature range 23-266°C and explained several salient features of ac conductivity and extracted physical parameters like \( dc \) conductivity, activation energy for dc conductivity, hopping frequency and energy for the formation of defects.

The common ac conductivity characteristics of vast majority of ion conducting solids are\(^{19-22}\):

(a) At low frequency, real part of the conductivity, \( \sigma '(\omega) \), is frequency independent.

(b) Around the cross-over frequency, \( \omega _n \), the ac conductivity sets in, and for \( \omega > \omega _n \), the \( \sigma '(\omega) \), shows the frequency dependent power law, \( \omega ^n \), with exponent \( n<1.0 \) and concomitantly, the permittivity loss, \( \varepsilon ''(\omega) \), shows, \( \omega ^{-n} \).

(c) As the temperature is lowered or frequency is increased, the frequency exponent \( n \) goes to 1.0, and it is called nearly constant loss behaviour.

(d) In log-log plot, the ac conductivity is less temperature dependent than the \( dc \) conductivity.

Eq. (23) is used to study the \( dc \) conduction. The symbols in Fig. 4(a) show the log-log plot of \( ac \) conductivity data of single crystal of NaCl: (50 ppm Zn\({ }^{2+}\)) in the temperature range 23-266°C. The continuous lines in Fig. 4(a) are the least square non-linear fit with Eq. (23) and the symbols are positions of \( \omega _n , \omega _k , \omega _p , 1/\tau _R \) and \( 1/\tau _I \). This is the first proposed model to extract \( \sigma _0 \) from the \( ac \) conductivity data. Fig. 4(b and c) shows the temperature dependence of \( g \) and \( E_L \). The value of \( E_L \) is found to be a few meV.

The observations of common \( ac \) characteristics, (a)-(d), are explained using \( ac \) conductivity Eq. (23). The continuous lines in Fig. 4(a) are the least square non-linear fits with Eq. (23). The fit parameters, \( dc \) conductance \( G(0) \) or \( \sigma (0) \), fast and slow hopping frequencies \( \omega _p \) and \( \omega _p , 1/\tau _R \) and \( 1/\tau _I \). This is the first proposed model to extract \( \omega _0 \) from the \( ac \) conductivity data. Fig. 4(b and c) shows temperature dependence of \( g \), and the lattice heat bath energy \( E_L \). To ascertain the origin of dispersion in \( ac \) conductivity which is due to the slow and fast
hopping processes with coupling, correlation and bounce-back hopping, the dispersion curve at $T=127\degree C$ in Fig. 4(a) is considered for the further discussion. The important $ac$ characteristics, (a)-(d), listed in Fig. 4 are found with $ac$ conductivity given in Eq. (23). The magnitudes of fit parameter obtained for $T=127\degree C$ are: $G(0)=(8.11\pm0.34)\times10^{-11}S$, $\omega_p/2\pi=(2.64\pm0.41)\times10^4Hz$, and $g=0.645\pm0.009$. The slow hopping frequency is $\omega_p/2\pi=1.40\times10^6Hz$, and the bounce-back frequencies are: $\omega_b/2\pi=1.19\times10^6Hz$, $\omega_p/2\pi=7.41\times10^6Hz$, $1/\tau_c=1.65\times10^4Hz$, $1/\tau_p=2.66\times10^6Hz$. According to the model, $g=1$, implies the fast hopping process with random hopping frequency $\omega_p$ and $\Gamma^c=1$.

The $g=1$, $\sigma(0)\sigma(\omega_p)$, corresponds to fast random hopping with no correlation and memory effect in hopping dynamics and hence, there is no dispersion in $ac$ conduction.

The carrier density involved slow and fast hopping dynamics which are calculated using $g$ and $dc$ conductivity and results are shown in Fig. 5 as a function of temperature for the single crystal of NaCl:50ppm Zn$^{2+}$. Fig. 5 clearly shows the charge carriers involved in the fast and slow hopping dynamics. The point defects (vacancies) and the substitutional impurities Zn$^{2+}$ are the cause for the disorder. The relaxation of charge carries $qn_c$ is found to be short-time and relaxation of charge carriers $gqn_c$ and $(1-g)qn_c$ are found to be slow relaxation and both processes coupled and correlated in units of ionic charge $qn_c$ and coupling parameter $g$.

Around $\omega_p$, the dispersion in $ac$ conductivity sets in. The $g=0.645$ implies interactions between the distributed charges, $gqn_c$, and $(1-g)qn_c$, and therefore, the energy barrier $E_{H}$ becomes barrier energy $gE_{H}$. The magnitude of $E_{H}$ is found to be $0.65\pm0.02eV$ and it is found from Arrhenius plot of Fig. 6. The value of $g=0.645$, also implies, at thermal equilibrium, there is a thermally driven current-current fluctuations in the space charge decay due to $E_1$ with coupling between fast and slow hopping and correlation hopping frequencies $\omega_b$, $\omega_p$, $1/\tau_c$, and $1/\tau_p$ in the slow hopping process. The slow hopping conductivity $\sigma(\omega_p)$, the slow hopping polarization and correlation are responsible for the term $\sigma(0)\omega_p\tau_1$ in Eq. (23). The $dc$ conductance, $G(0)$ or $dc$ conductivity $\sigma(0)$, and the fast hopping frequency, $\omega_p$, are thermally activated and increase with increase of temperature and follow Arrhenius Eqs (7) and (15). Fig. 6 shows Arrhenius plot of $\sigma(0)$, $\omega_p$ and temperature dependence of $\omega_p$.

The activation energy $E_{H}$ for fast hopping frequency $\omega_p$ and activation energy $E_\sigma$ for $dc$ conductivity $\sigma(0)$ or $dc$ conductance $G(0)$, are found to be $0.65\pm0.02eV$ and $0.87\pm0.03eV$ for NaCl:Zn$^{2+}$. The difference

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**Fig. 4 — (a) Log-log plot of $ac$ conductance data of single crystal of NaCl: (50 ppm Zn$^{2+}$) in the temperature range 298-475 K. The continuous lines are the least square non-linear fit to Eq. (23). Fig. 4(b and c): The $g$ and $E_1$ as a function of temperature. The symbols (online colour) are positions of correlation times, rates and $\tau$.

**Fig. 5 — Fast hopping process carrier density $N=qn_c$, slow hopping process carrier densities $M_p=3qn_c$, and $M_p=2qn_c$ obtained from the $dc$ conductance data of single crystal of NaCl: (50 ppm Zn$^{2+}$) for different temperatures.

**Fig. 6 — Arrhenius plots of $dc$ conductance, $\sigma(0)$, fast hopping frequency $\omega_p$ and inset shows temperature dependence of slow hopping frequency $\omega_p$ for single crystal of NaCl: (50 ppm Zn$^{2+}$) in the temperature range 298-533 K.
between $E_a$ and $E_B$ is found to be 0.22±0.02eV and it is equal to energy for the formation of defect $E_d$.

The magnitude, $\sigma(0)\omega_0$, to be added to the $\sigma(0)$ at a given temperature is decided by the fast hopping frequency $\omega_p$, $g$, the slow hopping frequency and correlation. The various symbols shown on the dispersion curve in Fig. 4(a) are the magnitude of conductance, $G(\omega)$ or conductivity $\sigma'(\omega)$, evaluated at $\omega=\omega_p$, $\omega_0$, $\omega_p^g$, $1/\tau_p$, and $1/\tau_d$, respectively for different temperatures, and these points lie around region where there is dispersion in conduction. The $\omega_p$, $\omega_0$, $\omega_p^g$, $1/\tau_p$, and $1/\tau_d$ are the allowed hopping frequencies in the fast and slow polarization in the relaxation function $\phi(t)$.

Weakly defective single crystals NaCl:(50 ppm Zn$^{2+}$) are molecular type disordered system. They contain a relatively large fraction of disorder due to the incorporation of the bivalent additive Zn$^{2+}$ in the case NaCl:Zn$^{2+}$. These centers are trapping centers of mobile hopping charge carrier $q\tau_c$. The presence of such large centers complicates considerably the fast hopping charges relaxation kinetics and the model provides the description of this until their latest stages where slow hopping kinetics takes over. The random fast relaxation dominates at the very earliest stages of relaxation and subsequently the non-random correlated long time slow relaxation, where memory effects are important in units of fast hopping ion charge with coupling and correlations in terms of $g$. It is clear that the simple doped system where the part of atomic or molecular framework is essentially fixed and the relaxation involves only in terms of single and continuous process of polarization and relaxation of hopping charge carriers. The proposed model has been further extended to investigate the $ac$ electrical properties of polycrystalline, glassy solid ion conductors and results show good agreement with observations.

7 Conclusions
The $ac$ conductivity and dispersion in $ac$ conductivity are shown to be delayed triggering of slow hopping frequency $\omega_p^g$ with respect to the fast hopping frequency $\omega_p$. The physical origin for the delayed triggering of slow hopping process is due to the trapping of mobile hopping charges carriers and their correlation. The $ac$ conductivity spectra analysis with present model provide physical parameters of materials namely, $dc$ conductivity, $ac$ conductivity, activation energies for $dc$ conductivity and hopping frequency. The existing phenomenological and empirical models, the physical process of polarization and relaxation are ambiguous in terms of exponent $\beta_{aw}$, $\alpha$, $\beta$, $n$. The proposed polarization mechanism and the complex current response function appear to be an alternate for polarization current response function with several remarkable physical features in terms of the exponent $g$. Therefore, the coupled slow and fast hopping model may find applications in electrical characterization wide variety of disordered solids.

Acknowledgement
Financial support from the UGC-SAP F.530/15/DRS/2009 is gratefully acknowledged.

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