Dielectric response of centrosymmetric $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ crystals in a low-frequency range

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Abstract. The dielectric response (DR) of centrosymmetric (space group, *Ibam*, at 293 K) $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ single crystals has been studied in a wide temperature range 290–700 K and frequency interval $5-5 \times 10^5$ Hz. The DR reveals dipolar features. The corresponding dielectric relaxation has a non-Debye character. As a consequence, the frequency dependences of both ϵ' and ϵ'' can be fitted with a stretched-exponent approach. The value of the stretched exponent p significantly depends on temperature, exhibiting two peaks: the first peak is at the glass–crystal transition in the sodium subsystem of the crystal and the second peak is above the phase transition point to a modulated phase.

1. Introduction

The dielectric response (DR) of superionic conductors has attracted much attention in recent years (see, e.g., [1] and references therein). However, usually only the high-frequency ($f \geqslant 10^5$ Hz) DR has been the subject of much concentrated consideration. The low-frequency DR of these materials has not received much study.

This is primarily because of the widespread opinion that the phenomena occurring at the electrode–electrolyte interface dominate the observed low-frequency DR of the crystals. In such a case, thorough consideration of the contribution of these interfacial processes needs some additional suggestions. This, in turn, results in many descriptive parameters that gives many 'degrees of freedom' to the system. In other words, considering the interfacial processes as dominant, one can never be sure that the chosen set of corresponding parameters (e.g. the double-layer, geometrical and bulk capacitances, the bulk conductivity of the sample, and the characteristics of the non-linear elements) is the only set that allows one to fit the experimental DR.

However, from our point of view, this attributing *a priori* the low-frequency behaviour of the superionics to the interface-caused phenomena looks rather doubtful. Indeed, real crystals (or glasses) have a wide spectrum of various excitations, extending, at least, to the range of hundreds of hertz. These excitations can be caused, for example, by the structural or microstructural features of the crystal (the motion of the domain walls, the additional phonon modes due to the ordered distribution of these walls (quasi-lattice), the reorientation of relatively large structural units (molecules, and isolated complex anions such as SO_4 and PO_4), the dynamics of different clusters, and so on).

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All these phenomena are absent in liquids and melts. So they are rather unusual in the electrochemistry of liquid and melt electrolytes which provided the idea of the dominant role of processes at electrode–electrolyte surface in the physics of superionics.

Thus attributing the low-frequency behaviour of a solid electrolyte only to the interface phenomena always needs experimental confirmation (see, for instance, the discussion in [2]).

This paper presents data on the low-frequency DR of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ single crystals belonging to superionic conductors with charge transfer due to motion of the sodium ions [3]. The aim of this work is to find the origin of the low-frequency anomalies in the dielectric spectrum of the compound.

2. Experimental details

Single crystals of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ were obtained by the flux technique [5]. The chemical formula of the compound as well as its crystal structure were refined by x-ray diffraction [4].

The DR of the crystals was studied in the frequency range $5-5 \times 10^5$ Hz (Tesla BM 507) and temperature interval 290–700 K. Single crystals under investigation have a plate-like shape (approximately $2-5$ mm $\times$ $4-7$ mm $\times$ $0.4-0.8$ mm). Measurements were carried out with samples of different geometries to study the possible effect of the interfacial phenomena on the total DR of the electrochemical cell.

The heat capacity of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ has been investigated in the temperature range 290–600 K (Perkin–Elmer DSC-7).

3. Results and discussion

3.1. Frequency dependences of σ''

Figure 1 shows the frequency dependences of $\epsilon' \omega$ (i.e. σ'') for $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ (measurements along the [001] direction) within a log–log framework. This form of representation of the experimental data seems to be more convenient than the usual $\epsilon'(\omega)$-dependence. Indeed, in the case of a significant dipolar contribution to the total DR of a material, it transforms a shoulder in the the $\epsilon'(\omega)$-curve to a peak in the $\sigma''(\omega)$-dependence. As can be seen from figure 1, this peak is a distinguishing feature of the spectrum obtained over the entire temperature range.

The peak is broader than is predicted by the Debye model [6]. This is a usual phenomenon and there are many theoretical approaches trying to explain the non-Debye DR of solids (see, e.g., [1,7] and references therein). The presence of the peak itself indicates that there is a relaxation process in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ similar to dipolar reorientation. The frequency ω_p of the reorientation corresponds to the peak frequency. It should be noted that a positive slope is observed for some curves in figure 1 at higher frequencies than ω_p. This phenomenon could be due to another relaxation process in the crystal with $\omega'_p > \omega_p$.

In principle, the observed peak $\sigma''(\omega)$ could be due to processes at the electrode–electrolyte interface, e.g. the appearance of a charged double layer [7]. In this case, the peak parameters (FWHH, intensity, $\omega_{p'}$, etc) must depend on the geometry of the interface (its area, thickness and so on). Figure 2 shows the frequency dependences of the imaginary part of the ionic conductivity of the sample coated with graphite electrodes. The areas of the electrodes have different orders of magnitude for the two curves presented. Also, the
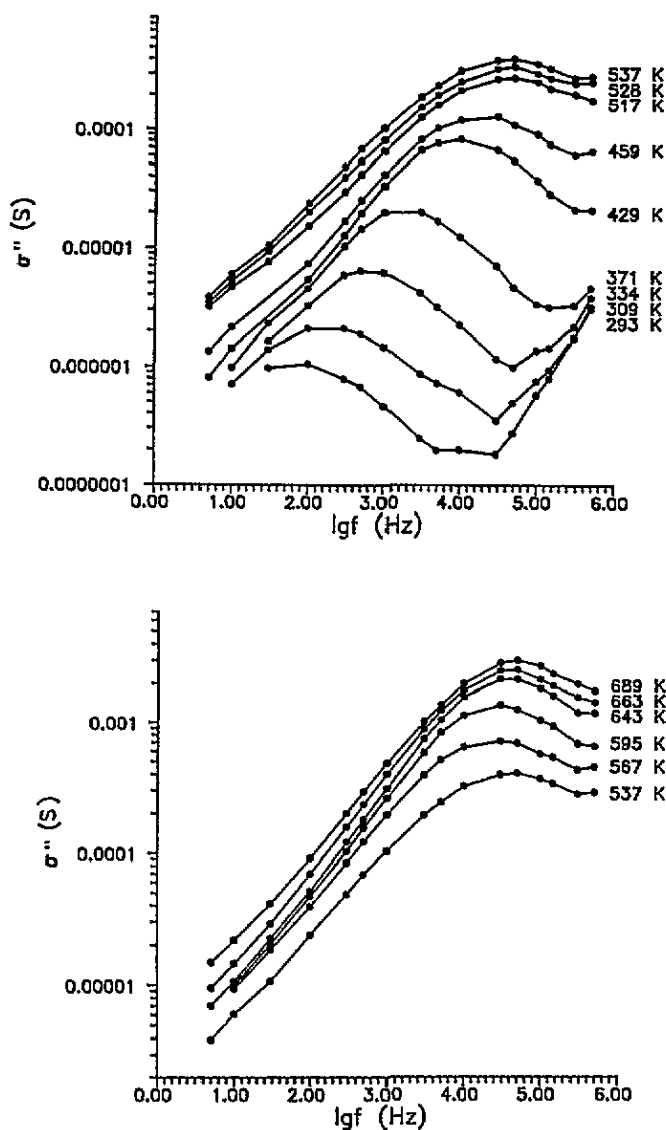
Figure 1. Frequency dependences of the imaginary part of the ionic conductivity of Na$_{4.6}$FeP$_2$O$_{8.6}$F$_{0.4}$ at various temperatures.

geometrical capacitance is greater for the sample with the larger square of the electrodes than for the sample with the smaller square of the electrodes.

So, if the dipolar peak is caused by the geometrical and double-layer capacitances, the curve indicated by open circles should lie above and to the right of the curve indicated by crosses. However, as can be seen from figure 2, the crosses lie significantly above the open circles and the values of ω_p are equal for these dependences. This result allows one to suggest that the contribution of the processes at the electrode–electrolyte interface to the total DR of the system is insignificant.

As can be seen from figure 1, the value of ω_p is rather low (about 10^3–10^5 Hz) over the entire temperature range. This indicates that the above-mentioned dipolar reorientation
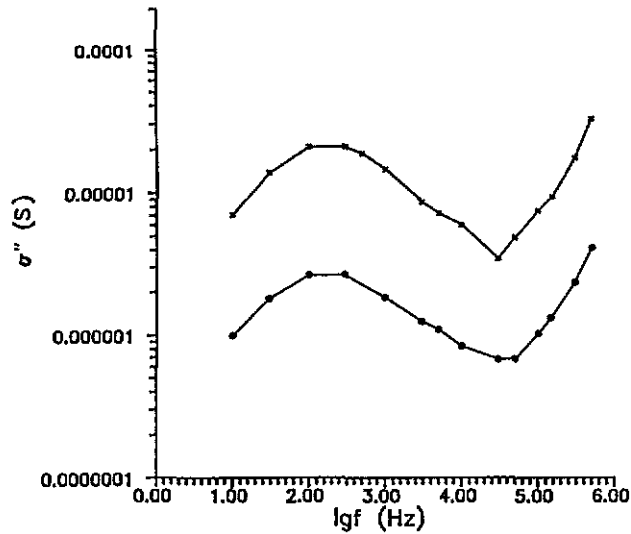
Figure 2. Frequency dependences of imaginary part of the ionic conductivity of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ where the S/l values indicated by open circles are much greater than the S/l values indicated by the crosses where S is the square of the electrodes and l is the thickness of the crystal between them.
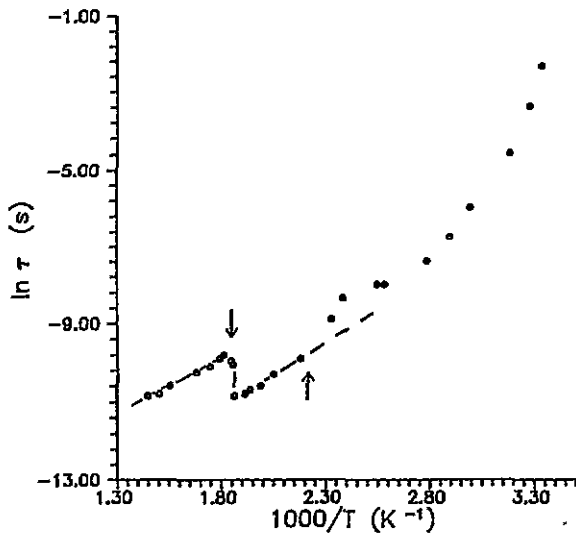

Figure 3. Temperature dependence of the reciprocal characteristic (peak) frequency ω_p^{-1} for σ'' in the Arrhenius format. Arrows indicate phase transition temperatures.

in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ is a relatively slow process weakly dependent on temperature. The temperature dependence of ω_p^{-1} (i.e. relaxation time τ) is presented in figure 3. It is of interest that the $\tau(T)$-curve does not obey the Arrhenius law below about 400 K. Instead the Vogel–Fulcher–Tammann (VFT) law ($\tau \propto \tau_0 \exp[-E_a/k(T - T_0)]$) [8–10] is fulfilled for the dependence ($T_0 = 260$ K, $\nu_{p0} = 1.79 \times 10^5$ Hz and $E_a = 0.03$ eV). The ($T - T_0$)

dependence is shown in figure 4. The value of activation energy E_a found is rather low in accordance with the above weak temperature dependence of ω_p.
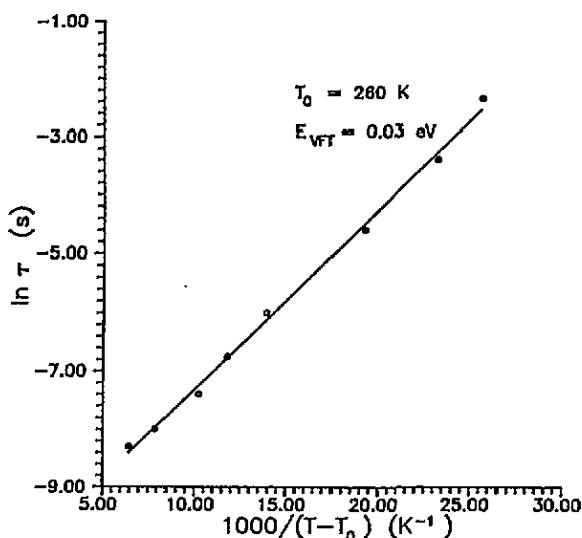

Figure 4. Temperature dependence of the reciprocal characteristic (peak) frequency ω_p^{-1} for σ'' in the VFT format (below 420 K).

VFT-law behaviour of relaxation processes is usually observed for glasses, supercooled liquids and polymers near the glass-transition point (α-relaxation [11]), where the 'viscosity' of a medium rapidly increases. In this case, T_0 indicates a temperature below which the 'viscosity' becomes infinitely high and a motion controlling the relaxation is 'frozen in'.

So, one can suggest that the dipolar reorientation found in Na$_{4.6}$FeP$_2$O$_{8.6}$F$_{0.4}$ becomes slower as the temperature approaches 260 K and disappears below this temperature. In other words, one can suggest that an orientational dipole glass appears in this compound below T_0.

It should be noted that it is rather complicated to define the structural mechanism of the dipolar relaxation. The reorientational process can be attributed, in principle, to reorientation of an 'effective' dipole. Such a dipole can be formed by either a sodium ion hopping in a double-well potential (or between two adjacent available sites) or rotating (librating) PO$_4^{3-}$ tetrahedra. Correspondingly, the glass state can appear in either the sodium of the PO$_4$ tetrahedra subsystem of the crystal. This problem will be considered in detail below.

Above about 420 K, ω_p increases with increasing temperature in accordance with the Arrhenius law (activation energy $E \simeq 0.28$ eV; $\nu_0 = 2.29 \times 10^7$ Hz). However, at about 545 K the characteristic frequency undergoes a stepwise decrease (see figure 3). These temperature intervals where $\omega(T)$ changes its behaviour are close to the temperatures of phase transformations of Na$_{4.6}$FeP$_2$O$_{8.6}$F$_{0.4}$: about 450 K and about 545 K [3]. The structural mechanism of the low-temperature phase transition is not yet clear (it will be discussed below) while the transformation at 545 K is a transition to a modulated phase [4]. Thus the latter phenomenon results in 'slowing' of the reorientational motion in the compound under consideration. With further temperature increase above 545 K, ω_p increases in accordance with the Arrhenius law ($E \simeq 0.24$ eV; $\nu_0 = 3.1 \times 10^6$ Hz).

3.2. Frequency dependences of σ'

The frequency dependences of $\epsilon''\omega$ (i.e. σ') are shown in figure 5. At any temperature the $\sigma'(\omega)$ curve consists of an almost frequency-independent part ($\omega > 10^4$–10^5 Hz) and a dispersive part ($\omega < 10^4$ Hz). The temperature behaviour of the dispersion is rather unusual. Indeed, as can be seen from figure 5, it increases with increasing temperature. At 293 K, σ' is almost frequency independent over the entire frequency range, i.e. $\sigma(\omega) \simeq \sigma(0)$. Then, the higher the temperature, the more distinct is the dispersion.

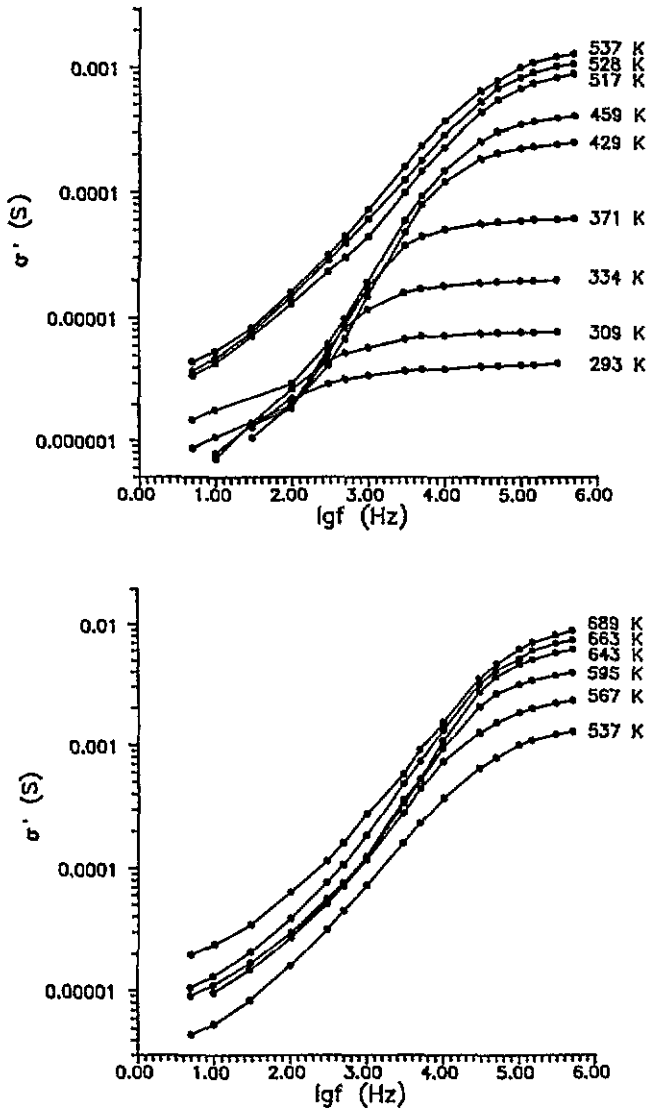**Figure 5.** Frequency dependences of the real part of the ionic conductivity of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ at various temperatures.

In general, the frequency dependence of the ionic conductivity of the compound obeys the well known empirical equation:

$$\sigma(\omega) = \sigma(0) + A\omega^p \qquad (1)$$

where A is a constant and $0 < p < 1$ [7]. The case when $p = 0$ corresponds to the classical Debye approach. Deviations from the Debye model increase with increasing p. It should also be mentioned that the parameter p is coupled to the stretched exponent β in the Kolraush–William–Watts function ($\varphi = \exp[-(t/\tau)^\beta]$), describing the corresponding dielectric relaxation rate: $p + \beta = 1$ [1]. Thus at $p = 0$ the time decay of polarization of the sample will follow the exponential law, while with increasing p the relaxation will become slower and vanishes at $p = 1$.
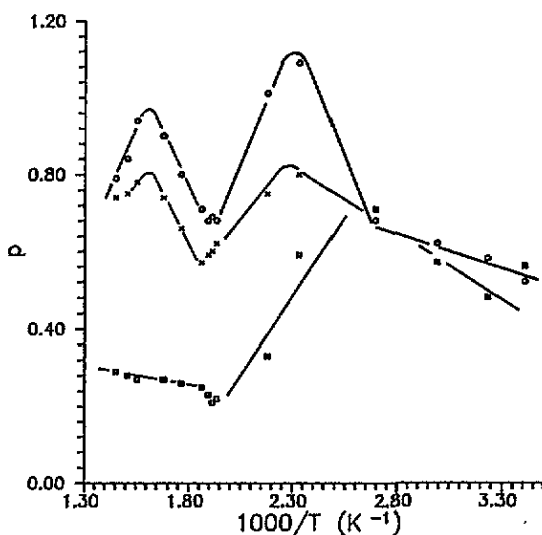
Figure 6. Temperature dependences of the dispersion index p for different frequency ranges: $\Box$, p_i^h; $\times$, p_i^l; $\bigcirc$, p.

Figure 6 shows the temperature dependence of the parameter p. As can be seen from figure 6, the $p(T)$-curve has a non-monotonic character. This is a rather surprising result. Indeed, in most conductive solids, p is a monotonically decreasing function of the temperature (see, e.g., [1, 7] and references therein). A few exceptions were found for solids undergoing a glass transition [12, 13]. In this case, the temperature dependence of p has a maximum in the vicinity of the glass transition point.

3.3. Phase transitions in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$

There are two maxima (at about 430 K and about 650 K) in the $p(T)$-dependence presented in figure 6. The temperature corresponding to the first maximum is close to the temperature of the low-temperature phase transitions in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ (about 450 K). The second maximum lies in the temperature range corresponding to the modulated phase.

As mentioned above, the origin of phase transformation at about 450 K is not yet clear. Figure 7 shows a DSC curve for a centrosymmetric $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ single crystal. There are two distinct anomalies in this curve. The strong endothermic λ-type anomaly at about 545 K ($\Delta C_p \simeq 1.5$–2.5 J mol^{-1} K^{-1}) can be attributed to the phase transition into a modulated phase [4]. Another stepwise exothermic anomaly at about 450 K results
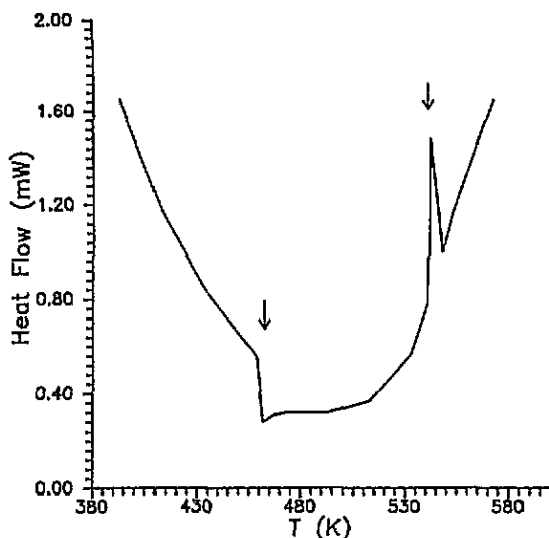
Figure 7. DSC trace of centrosymmetric $Na_{4.6}FeP_2O_{8.6}F_{0.4}$; the arrow at about 450 K indicates an exothermic anomaly of the specific heat ('recrystallization'), and the arrow at about 545 K indicates the phase transition to a modulated phase.

in a shift in the DSC curve and a change in its slope. The shape of the latter anomaly is quite similar to that predicted by the Landau theory [14] for the case of strong correlation between the displacements of all atoms. Such a situation can be observed, for example, in the appearance of (or variation in) long-range order in the system. For instance, a stepwise exothermic behaviour of $C_p(T)$ has been found for a phase transition from an incommensurate to a normal phase in $Ba_{0.1}Na_{0.9}Nb_5O_{15}$ [15] and for a ferroelastic phase transformation in $La_xPr_{1-x}P_5O_{14}$ solid solutions [16].

Thus we can suggest that atomic rearrangement occurs in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ at about 450 K. The above-mentioned transition from the α-type relaxation to the Arrhenius-law relaxation in the vicinity of this temperature indicates that the crystal becomes closer to the pure crystalline state above 450 K. In other words, this rearrangement corresponds to 'recrystallization' of the subsystem forming the orientational glass below 260 K. So, the observed increase in p in the vicinity of this transformation can be connected with this 'recrystallization'.

3.4. Model of the ionic motion in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$

One would like to propose the following simple model to account for the data obtained. In principle, as was mentioned above, the observed behaviours of both $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are similar to the behaviour of a composite material with an interface. This behaviour is rather frequently observed in studies of solids using dielectric spectroscopy (see, e.g. [7] and references therein).

In the case of homogeneous materials (single crystals, glasses and so on) this behaviour is, as a rule, regarded as a contribution of charge motion blocked at the interface (solid–solid boundary between the electrode and material in question).

However, as was shown above, the frequency dependences of ϵ^* found for $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ are not due to electrode effects. So, we can suggest that there are either intrinsic inhomogeneities in the crystal (for instance, twin boundaries) or another

microscopic mechanism resulting in the 'two-phase'-like behaviour of $\epsilon^*(\omega)$. Taking into account that there are no planar defects in these crystals in accordance with data from diffraction studies [4], we are inclined to believe that microscopic inhomogeneities exist in the samples. These inhomogeneities can arise as significantly different (on an energy scale) crystallographic positions composing the conductivity pathways for the motion of sodium ions.
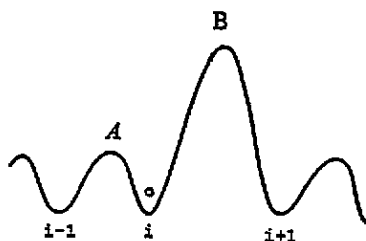

Figure 8. Schematic representation of a conduction pathway in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$.

Figure 8 shows schematically the model considered. Barrier A differs from barrier B. In such a case, when the migration path of an ion consists of a sequence of both barrier A and barrier B, the particle will be localized for a long time (with respect to the average time of migration given by $\tau^* = \tau_h + \tau_{r'}$ where τ_h and τ_r are the time of a hop and the residence time, respectively) at the A–B 'boundary'. A similar model has been suggested earlier to describe the ionic conductivity in LaF_3 [17].

Then the microscopic mechanism of the dispersion of σ can be accounted for in terms of the Funke theory of jump relaxation [1]. Indeed, owing to the distinct inequivalence of barriers A and B, it is more probable that the sodium ions will make a backward hop from i to $i - 1$ well after a forward hop from $i - 1$ to i. Thus an ion will oscillate between the i and $i - 1$ positions. This will result in $p = 1$ (i.e. there is no relaxation). These oscillations can be considered as a reorientation of the effective dipole $i/i - 1$.

This approach may be used for $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ because of the distribution of the sodium ions in this compound over six crystallographically independent positions [4]. The nearest-neighbour surroundings of sodium ions in these positions differ significantly from each other. To pass through the lattice cell in any direction an ion has to go through several types of site. So, potential barriers between the sites composing the migration pathway can differ, leading to the observed frequency behaviour of the DR.

Within the approach the glassy state of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ should lead either directly (randomization of the spatial distribution of the sodium ions in the case of glassy state in the sodium subsystem) or circumstantially (randomization of the nearest surroundings of Na^+ ions in the case of PO_4 orientational glass) to more equivalent Na^+ sites with respect to the crystalline state. This will result in small values of p in the glassy state (below about 420 K). With increasing temperature the compound undergoes structural relaxation to a 'perfect' crystal. As a consequence the Na^+ sites become more and more inequivalent in accordance with the average symmetry of the crystal. This process has a climax at about 450 K, i.e. at the 'recrystallization' temperature. So, the parameter p has to exhibit its highest value in the vicinity of 450 K (see figure 6). Above 450 K the inequivalency of the sodium sites is almost a constant parameter because the 'recrystallization' is finished. Thus the effect of the site inequivalency on the ionic motion is gradually decreased owing to an increase in the thermal energy of the moving ions with increasing temperature.

The modulation of the sodium sublattice appearing above 545 K means a new significant inequivalence among the sodium sites. Thus the parameter p has to increase (see figure 6). It is interesting to note that the second maximum on the $p(T)$-dependence is observed at a temperature (about 650 K) close to the temperature of 'saturation' in the itnensity of the satellite peaks in the diffraction pattern for the modulated phase of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ (about 630 K) [4]. This result confirms the existence of a relationship between the inequivalency of the crystallographic sites composing the conductivity pathways and the DR of the subsystems of ions moving over these sites.

It is noteworthy that the magnitude of the imaginary part of the dielectric constant remains almost the same within the temperature intervals corresponding to the maximal values of p for $\epsilon''(\omega)$ (see figure 5). These temperature-independent dielectric losses are the feature of DR of a rigid lattice [7]. So, this result indicates blocking of the mobile ions in the crystal. This may also be considered as additional confirmation of the suggested model.

3.5. Description of the DR of $Na_{4.6}FeP_2O_{8.6}F_{0.4}$

An effect of the blocking motion of charge carriers on the total DR of solids has been studied elsewhere [7] within the approach of the 'universal' DR. It was shown that the blocking-caused response will dominate the dielectric spectrum at low frequencies. This leads to the same slope of both the $\epsilon'(\omega)$- and the $\epsilon''(\omega)$-curves (about $-1 + p_i$ in the log–log framework, where p_i is the stretched exponent characterizing the dielectric dispersion at the 'interface'). With increasing ω, a significant contribution appears from local ion hopping. This results in an increase in the slope for the curve of log ϵ' versus log ω up to a value of about $-1 - p_i$, while the slope of log ϵ'' versus log ω has a constant value of about -1.

This model fits the experimental data obtained for $Na_{4.6}FeP_2O_{8.6}F_{0.4}$ well only at relatively low temperatures (below 400 K). Above this temperature the value of p_i obtained from the low-frequency wing of the $\epsilon'\omega$ peak (p_i^l) is significantly higher than that obtained from the high-frequency wing of the same peak (p_i^h) (see figure 6). Moreover, both these values of p_i differ from the corresponding value of p calculated from the frequency dispersion of $\epsilon''\omega$ at the same temperatures.

With further temperature increases above about 650 K the difference decreases between the values of p_i^l and p (see figure 6). On the other hand, above about 440 K, the value of p_i^h is still much lower than predicted by the Jonscher model.

From our point of view the observed deviations from the Jonscher model are due to the presence of two bonded processes in $Na_{4.6}FeP_2O_{8.6}F_{0.4}$; the first process is the motion of the sodium ions (either translational or reorientational in the case of effective dipoles) and the second process is librational motion of the PO_4 tetrahedra. In this case the observed DR will be a superposition of the dielectric responses corresponding to the processes mentioned (see figure 9). Then the value of p_i^l will be due to reorientational motion of the effective dipole (p_{d1} in figure 9), while the value of p_i^h will correspond to reorientational motion of the PO_4 tetrahedral (p_{d2} in figure 9).

This model internally requires strong correlation between the orientational motion of the both dipoles (to obtain close values of ω_p). Thus this approach is related to the well known 'paddle-wheel' mechanism of ion transport in solids [18]. However, it should be stressed that the above-mentioned correlations do not mean direct transport of the sodium ions by librating tetrahedra as suggested by the classic 'paddle-wheel' approach. A qualitative conclusion can be made only on the basis of the presented data; the probabilities of forward–backward (or forward–forward) hops should depend on the orientation state of the nearest PO_4 tetrahedra.
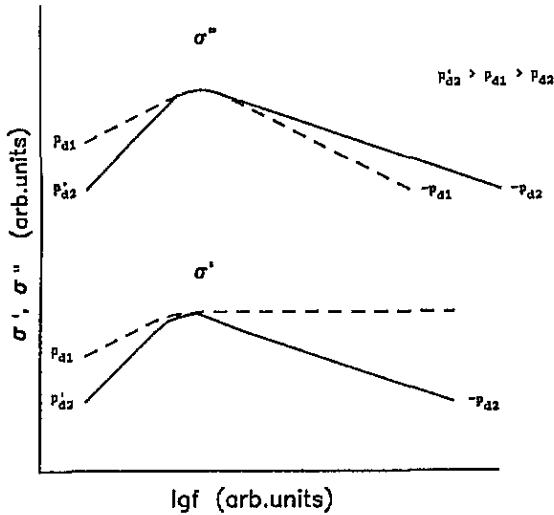
Figure 9. Schematic representation of the total DR for two parallel processes: - - - -, translational ionic motion with trapping and consequent local motion at the A–B 'boundary'; ———, pure reorientational motion of the PO$_4$ tetrahedra.

4. Conclusions

Thus the low-frequency DR of a centrosymmetric Na$_{4.6}$FeP$_2$O$_{8.6}$F$_{0.4}$ single crystal is due to a dipolar-type process. This phenomenon arises from the trapping of the mobile sodium ions at the 'boundary' between significantly inequivalent crystallographic sites composing the conductivity channels. This inevitably leads to the conclusion that the DC conductivity of the crystals is low. So the plateau observed in the $\sigma'(\omega)$-dependence at relatively high frequencies corresponds to local ionic motion between the traps.

Motion of the Na$^+$ ions can be coupled with a secondary dynamic process in the crystal: librations of the PO$_4$ tetrahedra.

With decreasing temperature a glass-like state appears in the sodium subsystem of the compound ($T_g \simeq 260$ K).

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