

## AC CONDUCTIVITY SPECTRA OF KCl CRYSTALS. TEMPERATURE DEPENDENT DEVIATIONS FROM THE SUMMERFIELD SCALING

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The application on the Summerfield scaling law does not lead to a superposition of the conductivity isotherms of KCl:In crystals, but the isotherms are shifted to higher values on the  $\frac{\nu}{\sigma_{dc}T}$  axis as the temperature decreases. The isotherms, however, do collapse onto a single master curve when an additional scaling factor  $T^\alpha$  with  $\alpha \in [1.2 \div 1]$  is used for frequency axis. The exponent  $\alpha$  decreases with temperature. The results of this scaling procedure have been obtained considering the shape of the isotherms being independent of composition.

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### 1. Introduction

Electrical and mechanical spectroscopy are two common methods for the study of the dynamical processes in solid and liquid materials. In many cases, it has been found that electrical and mechanical spectra obey the time-temperature superposition principle (TTSP), i.e., the spectral shape is independent of temperature. The validity of the TTSP suggests that the basic microscopic mechanisms of the dynamic processes do not depend on temperature, although the time window of these processes exhibits generally a strong temperature dependence.

The electrical conductivity spectra reflect thermally activated movements of charge carriers in a solid ionic and electronic conductor matrix, such as inorganic crystals, glasses, polymers, semiconductors. The TTSP principle is true in the low-frequency regime below a few MHz. The ion conducting solids may be considered as strong electrolytes where most if not all of the cations are mobile, or as weak electrolytes where the fraction of mobile ions is some function of temperature and composition. These observations must receive much attention since they impact strongly on the assessment of the theoretical approaches to charge transport and to relaxations occurring across the whole field of solid state ionics [1-4]. On short time and length scales, the mobile ions show a subdiffusive behaviour, i.e., the mean square displacement ( $\langle r^2(t) \rangle$ ) increases sublinearly with time, while on longer time and length scales, the subdiffusive behaviour passes over into a diffusive behaviour with  $\langle r^2(t) \rangle \sim t$ . Indium nanoparticles embedded in KCl crystals have been studied, recently, by Polosan et al. [5,6].

For a theoretical description of the ion dynamics in a structurally disordered ionic conductor, one often considers the hopping dynamics of non-interacting or interacting particles in disordered potential landscape. The short-time subdiffusive motions does not allow specific conclusions on the shape of the disordered potential landscape or on the role interionic interactions play in the ion dynamics. In order to obtain information of interionic interactions, detailed analyses of the frequency, temperature and composition dependence of the ac conductivity spectra of ionic conductors are necessary. The scaling method for the ac conductivity is a way developing the features of interest

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about these problems. Using of the scaling method consists to choose of a function depending of frequency, temperature and composition for the frequency axis, so that the isotherms of the real part of the conductivity  $\sigma'(\nu)$  do collapse onto a single master curve indicating an universal ionic relaxation process.

## 2. Scaling properties of conductivity spectra

In the first comprehensive analyses the validity of the TTSP, particularly in single ion conducting glasses has been confirmed by the following scaling law

$$\frac{\sigma'(\nu)}{\sigma_{dc}} = F\left(\frac{\nu}{\nu_0}\right) \quad (1)$$

here  $\sigma_{dc}$  denotes the dc conductivity, while  $\nu_0$  is a characteristic frequency defined by some authors that onset frequency of the conductivity dispersion  $\nu^*$  by  $\sigma'(\nu^*) = 2\sigma_{dc}$ , and have used  $\nu^*$  as a scaling parameter for the frequency axis.

The Summerfield scaling law [5], expressed by

$$\frac{\sigma'(\nu)}{\sigma_{dc}} = F\left(\frac{\nu}{\sigma_{dc}T}\right) \quad (2)$$

has the main advantage to utilize directly available quantities as scaling parameters for the frequency axis instead of an arbitrarily determined parameter  $\nu^*$ . In the diffusive dynamics,  $\langle r^2(t) \rangle$  increases linearly with time, so that  $\langle r^2(t) \rangle = D_0 t$ . Here  $D_0$  denotes the coefficient of self-diffusion of the mobile ions which is related to the dc conductivity via the Nernst-Einstein relation,  $\sigma_{dc} T = N q^2 \frac{D_0}{k_B}$ ,  $N$  and  $q$  being the number density and the charge of the mobile ions,

respectively, while  $k_B$  is Boltzmann's constant. This assumption is valid at low number density of mobile ions,  $N \leq 10^{20} \text{ cm}^{-3}$ , when the mobile particles does not interact via long-range Coulomb forces. The scaling function  $F$  is independent of temperature. Only the single alkali glasses ( $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O} \cdot \text{GeO}_2$ ) seem to obey equation (1), while the conductivity spectra of several mixed alkali glasses systems ( $\text{Li}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O} \cdot \text{Rb}_2\text{O} \cdot \text{B}_2\text{O}_3$ ) and alkali tellurite glasses ( $\text{Na}_2\text{O} \cdot \text{TeO}_2$ ) [6] cannot be superimposed by applying the Summerfield scaling law. The application of the Summerfield scaling does not lead to a superposition of the isotherms, but

isotherms are shifted to higher values on the  $\frac{\nu}{\sigma_{dc}T}$  axis as the temperature decreases. The

isotherms, however, do collapse onto a single master curve when an additional scaling factor  $f \sim T^\alpha$  with  $\alpha = -1.3$  is used for frequency axis [7]. This scaling law is founded in the random barrier model (RBM) without Coulomb interactions between the mobile ions. In this system, the

average interaction strength between the particle is the ratio  $\frac{V}{E_{\max}} = \frac{q^2}{4\pi\epsilon_0\epsilon_{\text{eff}}a} \frac{1}{E_a}$ . Here,

$V = \frac{q^2}{4\pi\epsilon_0\epsilon_{\text{eff}}a}$  denotes the Coulomb's interactions between the particles,  $\epsilon_0$  and  $\epsilon_{\text{eff}}$  are the permittivity of free space and an effective permittivity, respectively. Distance "a" depends on the

concentration of the particle, defined by the fraction of site occupied by particles,  $c \sim x^{-1/3}$  [8].  $E_a$  is the energy barriers between occupied sites. The scaling law with the expression

$$\frac{\sigma'(\nu)}{\sigma_{dc}} = f\left(\frac{\nu}{\sigma_{dc} T} T^\alpha\right) \quad (3)$$

is a theoretical result, the scaling procedure according (3) holds for alkali tellurite glasses, but with  $\alpha$  positive and strongly depending on the type of the alkali ion and on the alkali oxide content [8]. Experimentally  $\alpha$  decreases with increasing alkali oxide content.

On the other hand, at high concentration of the mobile ions (e.g.  $N \sim 10^{22} \text{ cm}^{-3}$ ), act the Coulomb interactions between the mobile alkali ions. The strength of these interactions characterized by  $V$ , increases with the alkali oxide content. Therefore, with increasing strength of the interactions in the RBM model (i.e., with increasing ratio  $\frac{V}{E_a}$ ),  $\alpha$  increases. This is a major contrast between theoretical and experimental results.

A positive value of  $\alpha$  implies that the  $\langle r^2(t) \rangle$  where the subdiffusive ion dynamics passes over into the diffusive dynamics increases with temperature. This fact suggests that the interionic Coulomb interactions are not the decisive factor determining the scaling properties of the ac conductivity spectra and that likely the number of available diffusion pathways decreases with increasing temperature.

### 3. Results and discussions

This paper shows the scaling properties of the conductivity spectra in KCl crystals. The isotherms of the real part of the conductivity  $\sigma'(\nu)$  have been obtained in the  $(10^2 \div 1.4 \times 10^6)$  Hz frequency range and  $(300 \div 500)$  K temperature range. Because the discussions are based on the log-log dependence of the conductivity on frequency, in Fig. 1 these isotherms are plotted in the onset frequency of the conductivity dispersion range.

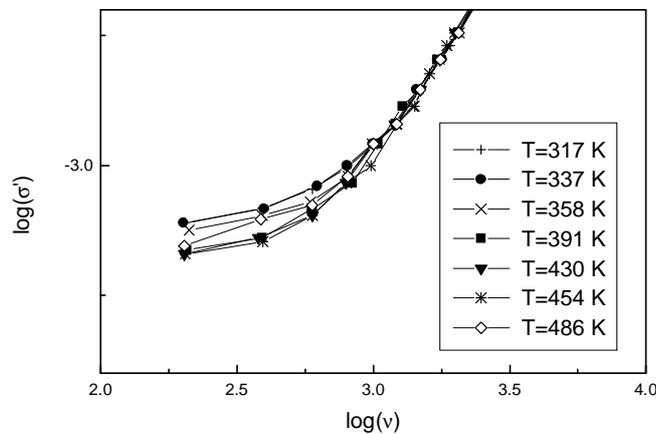


Fig. 1. Conductivity isotherms of KCl crystals.

Although in the crystals, as e.g. alkali halides, the ionic conductivity is controlled by vacancy dynamics, the spectral shapes of the conductivity of the KCl crystals and of other materials

(single alkali glasses, other inorganic crystals, polymers, semiconductors) are similar. In Fig. 2. are presented the isotherms of the  $\sigma'(v)$  of the KCl crystals scaled according the Summerfield scaling law (2). Obviously, the application of the Summerfield scaling does not lead to a superposition of the isotherms, but the isotherms are shifted to higher values on the  $\frac{v}{\sigma_{dc}T}$  axis as the temperature decreases. The isotherms, however, do collapse onto a single master curve when an additional scaling factor  $T^\alpha$  with  $\alpha \in [1.2 \div 1]$ , is used for the frequency axis, Fig. 3. The exponent  $\alpha$  decreases with temperature. It is important to note that the shape of the resulting master curve do differs on those of the original isotherms and that the frequency range for the master curve is diminished to the vicinity of the onset frequency of the conductivity dispersion. Consequently, it has been concluded that the ion and defect dynamics are important only below  $\sim 0.5\text{MHz}$ , while the electron dynamics are prevalent for higher frequencies. Therefore, the scaling procedure (3) remove the deviations from the Summerfield scaling with positive values for  $\alpha$  and that decrease with increasing temperature.

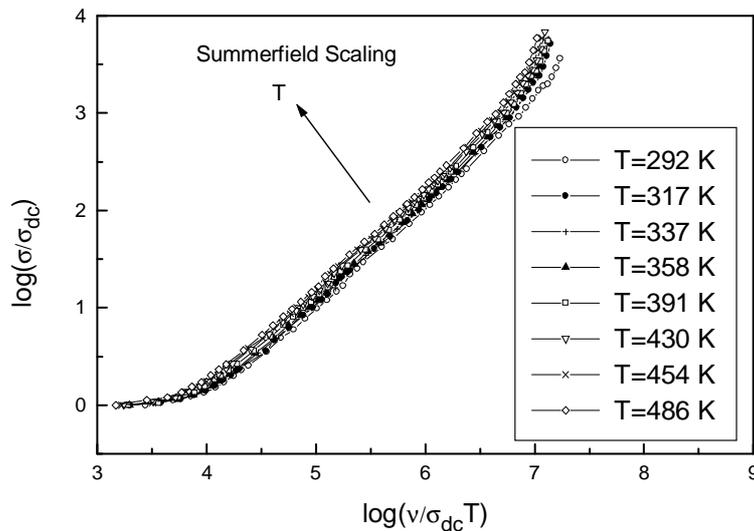


Fig. 2. Conductivity isotherms scaled according to the Summerfield law.

The electrical and optical properties of the alkali halides crystals are governed by structural defects: cation or anion vacancies, impurities and interstitial atoms. In the system of the KCl crystal with stabilized defects one may consider that the mobile particles [stabilized defects] are localized on well-defined sites with equal energies (because the matrix is crystalline) and that the heights of the barriers between these sites are spatially uncorrelated random variables (RBM model). Recently, Sidebottom [9] demonstrated that, in ion conducting crystals, the shape of the conductivity spectra depends strongly on the local dimensionality of the diffusion pathways. Thus, the scaling procedure results for KCl crystals can be analysed with the arguments from Section 2, i.e.,  $\alpha$  is positive and decreases with increasing temperature via decreasing the number of available diffusion pathways. These results also agree with the temperature dependence of the concentration of donor defects obtained from the isothermal frequency dependence of the ac-conductivity by extending the theory of the ac-conductivity for the disordered compounds [10].

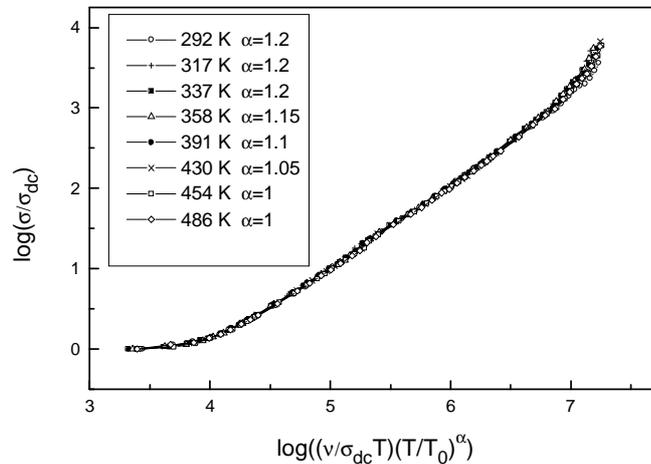


Fig. 3. Isotherms of the conductivity of KCl crystals scaled according to Eq. (3). The reference temperature  $T_0$  is 292 K.

#### 4. Conclusions

The results obtained from the scaling properties of the ac-conductivity spectra of KCl crystals are a new example of ion conducting materials displaying deviations from the Summerfield scaling. Although has crystalline (ordered) matrix, the analysis identifies the same structural feature being responsible for these deviations that for ionically conducting glasses (e.g., for tellurite glasses [6]). The isotherms  $\sigma'(\nu)$  collapse onto a single master curve when an additional scaling factor  $T^\alpha$  with  $\alpha$  positive and decreasing with increasing temperature via decreasing the number of available diffusions pathways.

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