Ionic thermocurrent in KCl doped with SO-24
D. Kostopoulos, S. Mourikis, P. Varotsos

To cite this version:
Journal de Physique, 1981, 42 (10), pp.1481-1483. <10.1051/jphys:0198100420100148100>. <jpa-00209340>

HAL Id: jpa-00209340
https://hal.archives-ouvertes.fr/jpa-00209340
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Ionic thermocurrent in KCl doped with SO$_4^{-2}$

D. Kostopoulos, S. Mourikis and P. Varotsos

Physics Laboratory, University of Athens, Solonos Str. 104, Athens-144, Greece


Résumé. — Les thermocourants ioniques (TCI) ont été mesurés dans des cristaux de KCl dopé avec K$_2$SO$_4$. Excepté pour une petite, mais très large bande à 215 K, on trouve deux bandes se recouvrant dont les maxima sont entre 240 et 255 K ; la bande à la température la plus élevée (246-255 K) est plus intense d’environ un ordre de grandeur. Cette bande intense correspond à une enthalpie de migration de 1,06 ~ 1,1 eV et à un facteur de fréquence préexponentiel très élevé $10^{18}$ ~ $10^{19}$ s$^{-1}$. L’autre bande semble avoir une enthalpie de l’ordre de 0,85 eV et un facteur préexponentiel de $10^{15}$ s$^{-1}$ environ.

Abstract. — Ionic thermocurrents (ITC) have been measured in crystals of KCl doped with K$_2$SO$_4$. Apart from a small but very wide band at 215 K there are two overlapping bands which have their maxima between 240 and 255 K ; the band maximizing at the higher temperature (246-255 K) is more intense by about one order of magnitude. This intense band corresponds to a migration enthalpy 1.06 ~ 1.1 eV and a very high preexponential frequency factor $10^{18}$ ~ $10^{19}$ s$^{-1}$ ; the other band seems to have an enthalpy around 0.85 eV and a preexponential factor of the order of $10^{15}$ s$^{-1}$.

It is extensively known [1] that in alkali halides an accurate determination of the defect parameters cannot be done by analysing only the conductivity data of a « pure » crystal. It is also necessary to know the conductivity of the same crystal when it is doped with small amounts of divalent cations and anions. Then a simultaneous computer analysis of conductivity measurements and those of diffusion can, in principle, lead to reliable set of parameters. In the case of KCl such an analysis has been carried out by Benière et al. [1] for the anion doping they have used K$_2$SO$_4$ and they found that the migration enthalpy $h^{m,-}$ and entropy $s^{m,-}$ for the free anion vacancy is 0.85 eV and 3.2 k respectively. In the same experiment the analysis showed that the migration enthalpy $h^{m,+}$ for the free cation motion is 0.73 eV : this latter value is comparable to those corresponding to a bound cation vacancy motion [2] obtained by the dielectric loss [3] or ITC (Ionic Thermocurrents) [4] techniques (provided that the ionic radius of the divalent cation dopant is not much smaller than that of K$^+$). Unfortunately, to the best of our knowledge, no value of the migration enthalpy $h^{m,b,-}$ for the bound anion vacancy in KCl has been published up to date. We have decided to measure the ITC spectrum of KCl + SO$_4^{-2}$ for two basic reasons :

(i) to determine its value of $h^{m,b,-}$ which seems to be absent in the literature and (ii) this crystal except of anion vacancies contains also (« free » and « bound ») cation vacancies because of the unavoidable existence of divalent cations ; therefore « vacancy-pairs » should be formed due to the electrostatic attraction of the free anion and cation vacancies. An unambiguous determination of the migration parameters of vacancy pairs remains today one of the most interesting problems in the study of transport properties of alkali halides because most workers [1] believe that they contribute significantly to the diffusion process of anions and cations.

1. Experimental. — The crystal KCl + 100 ppm SO$_4^{-2}$ (which has been grown from the melt) was mounted in a specially designed crystal holder between platinum electrodes. An electric field of about 5 kV/cm was applied on the crystal, at a temperature between - 10 and + 50 °C and then the crystal was cooled rapidly down to the liquid nitrogen temperature. The sample was then heated up to 50 °C at a rate 5.5-6.5 K/min. (the heating rate was kept constant during each run). The resulting depolarization current was measured with a Carry 401 electrometer ; it should be mentioned that special care had been taken for the (teflon) insulated connectors to be continuously at R.T. in order to avoid ITC currents from teflon.
2. Results. — Repeated measurements showed that the depolarization currents were more intense (by 1-2 orders of magnitude) when the crystal was preheated at 350-400 °C for a few hours.

Figure 1 shows a typical feature of the depolarization current observed in a preheated sample.

![Figure 1](image1)

The spectrum consisted of two main peaks. A wide peak at 240 K-255 K. Due to the fact that the wide peak was repeatedly observed by other workers and related to divalent cation impurities we have decided to clean it i.e. when the temperature of the sample reaches, approximately, 255 K, the sample was again cooled down to L.N. and then again the temperature was increasing with the constant rate. This cleaning procedure succeeded in eliminating the wide peak, lying at 230 K, was observed.

Figure 1 shows the spectrum when the cleaning procedure for the 215 K-peak has been applied. An inspection of the figure indicates a complex band with the maximum at 250 K and the remaining portion of the wide peak on the lower temperature side. It is stressed that the intense band showed in figure 1 was fairly reproducible in all the runs of the various samples used.

The depolarization current density $j$ — in the case of a single mechanism — obeys the relation:

$$ j = \frac{P_0}{\tau_0} \exp \left( - \frac{h_{m,b}}{kT} \right) \times $$

$$ \times \exp \left[ - \frac{1}{b\tau_0} \int_{\tau_0}^{T} \exp \left( - \frac{h_{m,b}}{kT} \right) dT \right] $$

(1)

where $P_0$ the « initial polarization », $b$ is the heating rate and $\tau_0$ the preexponential factor in the usual Arrhenius relation:

$$ \tau(T) = \tau_0 \exp \left( \frac{h_{m,b}}{kT} \right) $$

(2)

where $\tau(T)$ is the relaxation time for the reorientation process. The study of the function $j = f(T)$ shows that $j$ reaches a maximum at a temperature $T_m$ so that:

$$ \tau(T_m) = \frac{kT_m^2}{b h_{m,b}} $$

(3)

For temperatures appreciably lower than $T_m$, equation (1) simplifies to:

$$ j(T) = \frac{P_0}{\tau_0} \exp \left( - \frac{h_{m,b}}{kT} \right) $$

(4)

so that the slope of the plot $\ln j$ (or $\ln I$) vs. $1/T$ leads to a good estimate of the migration enthalpy $h_{m,b}$.

We have tried to describe the band shown in figure 1 in terms of equation (1); however we found that this band is more complex. A first attempt to analyse is as a sum of two ITC bands described by equation (1) was unsuccessful. It should be mentioned that the lower temperature part (~ 235-240 K) of this band (i.e. immediately before the shoulder shown in figure 1) when analysed in terms of (Eq. (4)) gives a « migration enthalpy » close to 0.85 eV and a preexponential factor $1.5 \times 10^{-16}$ s and $1.7 \times 10^{-15}$ s.

It is obvious that these values have a meaning only when we assume that the low temperature part of the band is well governed by one mechanism. However the fact that the resulting plot $\ln I$ vs. $1/T$ is linear possibly indicates that this part of the band is actually influenced by one mechanism.

Due to the complexity of the analysis of the band of figure 1 we have tried to « clean » the mechanisms (s) contributing to the low temperature region (i.e. the shoulder) of this band. After two « cleanings » we obtain the (single) band shown in figure 2.

An analysis of this band gives $h_{m,b} = 1.05 - 1.1$ eV and a preexponential factor $\tau_0$ which lies between $10^{-18}$ and $10^{-19}$ s. (The parameters given are from an analysis of 30 runs and do not correspond to the single case of figure 2.)

![Figure 2](image2)
These parameters are anomalous in two respects:

(1) the value of the migration enthalpy — if it corresponds to a bound anion vacancy motion — is about 20% higher than those reported for the free anion motion [1]. A second possibility is that it corresponds to a direct jump of $SO_4^{2-}$; in this case the value of 1.05-1.1 eV is not unreasonable but it seems a little difficult that the main reorientation process takes place through the jumps of $SO_4^{2-}$ which has a very high ionic radius. A third possibility is that this mechanism corresponds to the reorientation of vacancy pairs. We cannot preclude this possibility; among the others there is also the following difficulty to attribute this main peak to the reorientation process: the very high preexponential factor when expressed in terms of the migration entropy ($\tau_0^{-1} = 2 \omega_D \exp(sm/k)$ where $\omega_D$ is the Debye frequency) implies a migration entropy of the order of 10 k which is unusually high if one consider that the formation entropy \[7\] of a Schottky defect is of this order. However we are now doing experiments (with smaller concentration of $SO_4^{2-}$ i.e. smaller than the solubility limit [1]) in order to clarify if actually it corresponds to such a mechanism.

In summary we can state that the preliminary results on the ITC-spectrum of KCl + $SO_4^{2-}$ show the following:

(1) a plausible migration process with migration enthalpy close to 0.85 eV and a preexponential factor between $10^{-16}$ and $10^{-15}$ s. These values are, in principle, not far from those expected from a bound anion motion [1];

(2) a very intense peak close to 250 K which has a very high migration enthalpy (1.05-1 eV) and an unusually high migration entropy [8]. The unambiguous identification of this pronounced peak is not yet possible;

(3) a wide but not intense peak positioned at about 215 K. This may be related to the small amounts of divalent cations existing in the sample [5].

It should be mentioned that recent experimental results by Dryden and Meaking [8] indicate that the migration enthalpy of free anion motion in KCl is slightly higher than 1 eV. The latter value is similar to that of our main band. Thus indicating that this peak might be due to the reorientation of a dipole involving a bound anion vacancy motion.

References

[8] DRYDEN, J., private communication: recent experiments confirm that the migration enthalpy for the free anion vacancy is also a little higher than 1 eV.