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Defect kinetics in KCl single crystals

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Résumé. — Des mesures cycliques de la conductibilité ionique des cristaux KCl purifiés et adoucis montrent une mémoire des défauts thermaux au-dessous de 500 °C quand le taux de changement de température est égal ou supérieur de 1 °C par minute. Des études cinétiques suggèrent que le processus de décroissance peut être représenté par une réaction de décroissance bimoléculaire et une réaction de régénération monomoléculaire.

Abstract. — Cyclic measurements of ionic conductivity of annealed purified KCl crystals exhibit a thermal defect memory below 500 °C when the rate of temperature change is 1 °C min.⁻¹ or more. Kinetic studies suggest the decay process can be represented by a bimolecular decay and a monomolecular regeneration reaction.

The ionic conductivity at 1 kHz of annealed, purified KCl crystals was measured throughout several cycles of increasing and decreasing temperature. The analysis of these crystals has been reported elsewhere [1]. Spectrographic grade graphite was evaporated onto the crystal to form both the active and guard circuit electrodes. Acceptable electrodes have the appearance of vitreous graphite. The conductivity cell case and all internal supports were made of quartz. The cell is closed by a vacuum tight, water cooled nickel seal [2] through which all internal connections to the cell were made and which serves as the cell support. A large furnace mounted on tracks could be lowered or raised over the cell. Pt foils to which Pt wires were welded formed the electrical connections to the graphite electrodes. Temperature was measured by Pt/Pt-10 %-Rd thermocouples adjacent to the Pt foils and a similar thermocouple adjacent to the crystal was used to control the temperature.

Conductivity and capacity measurements were made on a General Radio 1673A/1672A bridge. The thermocouple voltage was digitized using a Hewlett-Packard 2212A voltage to frequency converter (10 mV = 150 kHz) and changed to a 8421 BCD code with a Monsanto 104A counter. The BCD data from these various devices passed through a locally constructed interface to a Gulton NP-7 printer. The interface could be programmed to select the quantities measured, the number of measurements during each sampling period, and to turn the furnace power off during measurement. A Barbra-Colman 540 and 621 SCR controller connected to a locally constructed electromechanical programmer was used to automatically increase or decrease temperature at the selected rate between preset limits.

Figure 1 shows a typical $\log \sigma T$ vs. $10^3/T$ plot for a series of 1 °C min.⁻¹ measurements (x first increase, □ first decrease, + second increase, △ second decrease). Below about 350 °C the furnace would

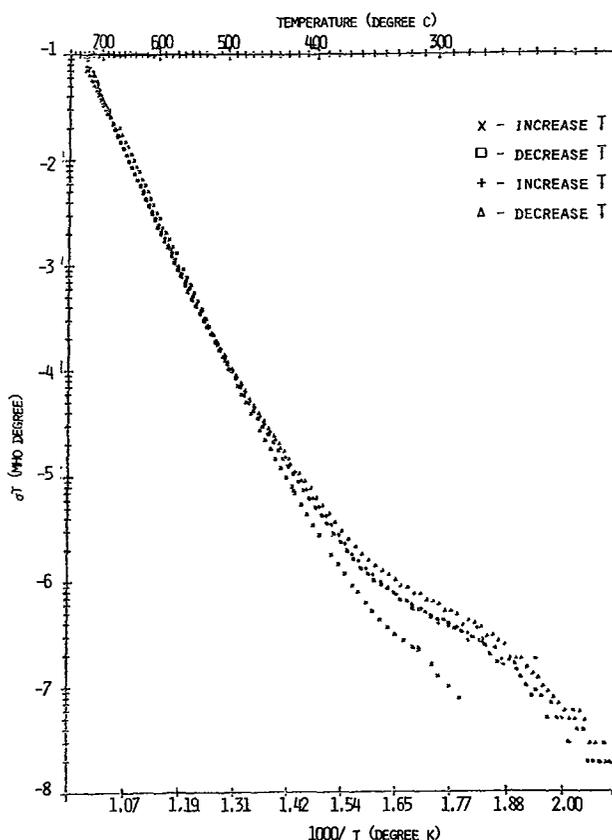


Fig. 1. — The conductance of purified KCl as a function of temperature. The crystal was initially well annealed (x). Cyclic temperature changes at 1 °C min.⁻¹ exceed the annealing rate of thermal defects at temperatures below 550 °C.

not cool as rapidly as $1\text{ }^{\circ}\text{C min.}^{-1}$ and at temperatures below $260\text{ }^{\circ}\text{C}$ the precision of σ measurements was poor. Here our interest is in the memory effect of the crystal of its thermal history. Clearly, temperature changes at the rate of $1\text{ }^{\circ}\text{C min.}^{-1}$ are too rapid for the defects to equilibrate at temperatures in the region of $500\text{ }^{\circ}\text{C}$ or lower. This observation led to a series of kinetic studies of the decay of σ at constant temperature in the temperature region near the onset of the effect. In these studies the sample was allowed to equilibrate at some high temperature T_2 . It is then cooled quickly to room temperature. The furnace is set at T_1 which is about 100° below T_2 . After a few oscillations the furnace and sample stabilize and σ is measured as a function of time as the crystal approaches equilibrium. The decay was studied between $475\text{ }^{\circ}\text{C}$ and $575\text{ }^{\circ}\text{C}$ at 25° intervals. The usual kinetic order analyses did not give integral reaction orders which indicates the process is complex. The decay curves (Fig. 2) could be represented by a

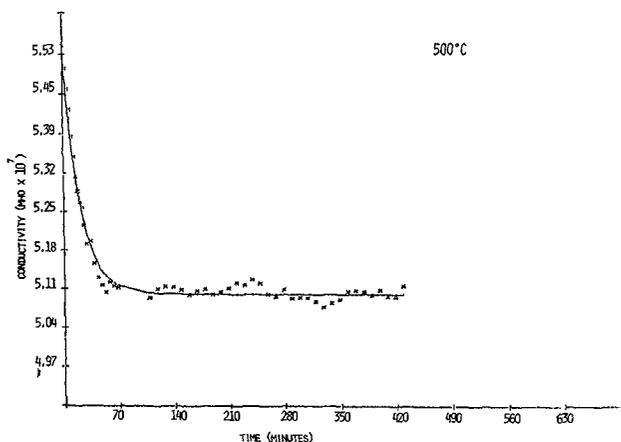


Fig. 2. — Experimental conductivity of KCl as a function of time at $500\text{ }^{\circ}\text{C}$. Solid line calculated from equation (1).

bimolecular decay and monomolecular generation of current carriers. If σ is proportional to the concentration of current carrying defects, such a process can be written as

$$-\left(\frac{\partial\sigma}{\partial t}\right)_T = k\sigma^2 - k'(\sigma_0 - \sigma), \quad (1)$$

where t is time, σ_0 the conductivity at $t = 0$, and k and k' are the rate constants for decay and formation of current carriers, respectively. For such a process the equilibrium constant K is given by

$$K = \frac{k}{k'} = e^{S/k} e^{-h/kT} \quad (2)$$

where h and S are the process enthalpy and entropy. In figure 2 the solid line is given by equation 1 with $k = 7.11 \times 10^3$ and $k' = 4.18 \times 10^{-2}$. Over this small temperature range $h = 1.61\text{ eV}$ and $S = 1.13 \times 10^{-3}\text{ eV/deg.}$ with a correlation factor of 0.957. At $475\text{ }^{\circ}\text{C}$ the conductivity decreases more rapidly than calculated by an equation of the form of 1. This suggests that more than one decay and regeneration process occurs simultaneously (i.e. $k = k_1 + k_2 \dots$) and the entropy of the processes differ substantially.

Kinetic data alone provides only necessary and not sufficient information to establish a model for any process. However these measurements indicate the decrease in conductivity occurs by several simultaneous reactions, such as vacancy pair formation, entrapment of vacancies on dislocations or other defects, etc. If several simultaneous reactions occur, the enthalpy of the overall process reported here should be less than that of any of the individual reactions. Further work is underway on doped crystals to attempt to separate these reactions.

References

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- [2] FREDERICKS, W. J., *J. Sci. Instrum.* **44** (1967) 561.