**07.3—2** THERMAL DISORDER AND THE IONIC MOBILITY TRANSITION IN HOLLANDITE. By Hans-Peter Weber and Heinz Schulz, Max-Planck-Institut f. Festkoerperforschung, Stuttgart 80, FRG

Hollandite-type phases are useful model structures for the study of ionic conduction because of the 1-dimensional nature of the diffusion path.

The structure of a synthetic hollandite with the composition $K_{1.54} Mg_{0.77} Ti_{7.23} O_{16}$ has been investigated at 133,293,387,459,540,707 and 919 K with a $(\sin \vartheta/\lambda)_{max}$ varying between 0.9 and 1.2 $Å^{-1}$. For $T \lesssim 387K$, electron-density maps in the plane of the c (tunnel) axis reveal a pattern of 3 superposed potassium peaks centered at approx. $0,0,\pm 0.25$ (terminal peaks) and $0,0,1/2$ (central peak). For $T \gtrsim 459K$, the height of the central peak decreases progressively in favor of the terminal peaks. A 3-atom model has been successfully refined for all temperatures, yielding the following structural details :

1) A plot of U_{33}(central atom) vs T displays a large discontinuity for $387K<T<459K$. This confirms the existence of a mobility transition for the tunnel cations as predicted from an extrapolation of the conduction behaviour determined for $T \lesssim 213K$ (Beyeler et al.,Phys. Rev Letters (1979) 42 819). When extrapolated to $T= 0K$, U_{33} has a positive intercept (0.42 $Å^2$), indicating that the central potassium site is a split-atom position.

2) Difference electron-density maps show a residual density at 0,0,0 (the bottleneck between 2 neighbouring cavities), which increases with temperature. Concomitantly, the bottleneck widens from 2.4 $Å$(T=133K) to 2.46 $Å$(T=919K) (Cf. the diameter of the diffusing ion, $2 \cdot r(K^{+1}) = 2.66$ $Å$).

3) The potential barrier between 2 cavities amounts to 48(5) meV. This value is in good agreement with an activation energy of 37meV obtained from conductivity measurements (Yokashido et al.,Solid State Ionics (1981) 5, 509) on a hollandite with a very similar composition.

4) As a corollary to the mobility transition, an inflection shows up in a plot of the cell constants vs T at $387K<T<459K$.
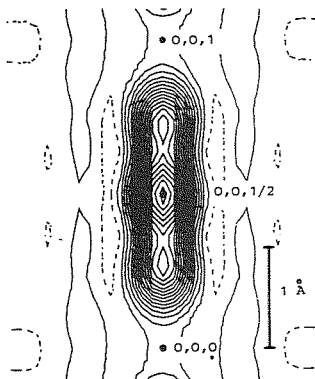
Fourier synthesis of the potassium electron-density in the plane ‖ (100) at 133K. Contours are plotted at 10 $e Å^{-3}$ intervals ; zero contour is omitted.

07.3—3 NETWORK ANALOGUE FOR A ONE-DIMENSIONAL SOLID IONIC CONDUCTOR. By G.Roth and H. Böhm, Institut für Mineralogie der Universität Münster. D-4400 Münster, Corrensstr. 24.

Impedance plots from single crystals of solid state ionic conductors often exhibit features which cannot be interpreted by standard concepts.

The common method of representing the electrical properties of a sample by an equivalent circuit which comprises a voltage generator, an ohmic resistor and two capacitors, is obviously not adequate for the majority of solid state ionic conductors.

In many cases boundary effects are responsible for the deviation from the expected behavior.

The objective of the present investigation is to outline the bulk effects of a single crystal which can be responsible for the observed anomalies in the impedance plots.

Based on a classical "hopping model" the jumps of overdamped particles between discrete positions are described by a system of coupled linear differential equations of first order ("master equation").

The analogue of this system of differential equations is an isomorphic system of equations describing the currents in an electrical network of voltage generators, ohmic resistors and capacitors.

The topology of this network is correlated to that one of the jump diffusion process in the crystal space.

One-dimensional single particle models can be represented as "active ladder networks", whereas one-dimensional multi-particle models lead to branched networks.

The values of the network components can be determined from the static properties of the model (e.g. the site occupancies in the field free equilibrium, the potential barriers etc.).

There is an unambiguous correlation between network components and microphysical processes in the crystal: The potential barriers correspond to the resistors, the potential minima to the capacitors and the voltage generators account for the potential change induced by the external field.

The proposed concept is applied to single- as well as multi-particle problems.

The results of the theoretical investigations of such networks are described and they are compared to experimental data.

In addition, the dependence of the impedance on various parameters of the model (e.g. ion concentration, interaction energy, potential distribution along the diffusion path etc.) is discussed.