

meters (a and c) increase monotonically with increasing temperature but the c axis of the  $Mg^{2+}-Li^+$  compound decreases rapidly between the temperature range  $100^{\circ}-220^{\circ}C$  and starts to increase above  $220^{\circ}C$ .

As yet there are not convincing proofs as to whether the anomaly in the thermal expansion should be attributed to phase transition as suggested by conductivity data or to a desorption of water from the interblock plane.

envisaged as associated in equal proportion in  $H_5O_2^+$  and  $H_4O_2$  dimers and this suggests a possible mechanism for proton conduction which can be probed by quasielastic neutron scattering.

For the single crystal neutron diffraction study of  $Sr(Pr)Cl_{2.10}$  ( $\lambda=0.53\text{\AA}$ ) it is demonstrated that the anion interstitials are of two types: ( $\frac{1}{2}vv$ )  $w=0.38$  and ( $xxx$ )  $x=0.285$ . The ratio of ( $\frac{1}{2}vv$ ) interstitials to dopant cations is about 2.5. In contrast to the alkaline-earth fluorides, ( $www$ )  $w=0.42$  or 0.38 interstitials are not important in this system. Defect energy calculations on anion-excess strontium chloride suggests that the clusters proposed for the alkaline-earth fluorides are less important for  $SrCl_2/MCl_3$ . Clusters based on the aggregation of  $\langle 111 \rangle$  cation substitutional/anion interstitial pairs provide a more favourable mode of defect cluster formation. A cluster model based on this type of aggregation provides a good model for our observed ratio of anion interstitials to dopant cations but does not explain the observed proportion of anion vacancies.

**07.3-06** NEUTRON DIFFRACTION STUDIES ON FAST ION CONDUCTORS (I)  $DUO_2ASO_4 \cdot 4D_2O$  and (II)  $Sr(Pr)Cl_{2.10}$ . By P. J. Bendall<sup>(i)</sup>, C. R. A. Catlow<sup>(ii)</sup>, B. E. F. Fender<sup>(iii)</sup> and A. F. Wright<sup>(iii)</sup>.

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Neutron diffraction studies are reported on two different types of fast ion conductor. In one, high resolution powder diffraction techniques are employed to detect hydrogen ordering effects and occupancies in the good proton conductor  $DUO_2ASO_4 \cdot 4D_2O$ ; in the other, a high resolution single crystal investigation has been used to accurately locate the chloride ion positions in the anion excess fluorite system  $Sr(Pr)Cl_{2+x}$ .

The isostructural layered hydrates  $HUO_2PO_4 \cdot 4H_2O$  (HUP) and  $HUO_2ASO_4 \cdot 4H_2O$  (HUAS) display high proton conductivities near room temperature (A. T. Howe and M. G. Shilton, J. Solid State Chem. (1980), **34**, 149). Profile analysis of  $DUO_2ASO_4 \cdot 4D_2O$  above the transition temperature of  $290 \pm 30K$  was carried out in the space group  $P4/ncc$  with  $a = 7.160$  and  $c = 17.634$ . The structure of DUAS is very similar to HUP, with planar networks of water molecules alternating with layers of  $\{UO_2PO_4\}_n^{n-}$ . The neutron diffraction study shows (i) only one of two crystallographically distinct sites in a square of water molecules is occupied by hydrogen atoms and the occupancy is  $3/4$ ; (ii) the hydrogen atoms directed towards the oxygen of an  $ASO_4^{3-}$  group are linked to the oxygen of a water molecule; (iii) the remaining hydrogen atoms (8 out of 36) are associated with a single maximum in scattering density midway between two oxygen atoms of water molecules in neighbouring water layers. The water molecules can thus be

**07.3-07** STRUCTURE INVESTIGATIONS IN FAST IONIC CONDUCTORS. By H. Schulz, MPI Festkörperforschung, 7 Stuttgart 80, Germany.

In fast ionic conductors one sort of ions may move rapidly through the crystal lattice. The densities of these ions are often distributed over large parts of the elementary cell. The smeared out densities are caused by shallow atomic potentials. These potentials are (at least in distinct directions) so flat, that already thermally activated ions may show large thermal vibrations or jump from their site into a neighbouring site.

The thermal vibrations of these ions may be analysed by so-called anharmonic temperature factors. The corresponding probability density maps can be calculated by the Fourier transform of the anharmonic temperature factors. These pdf maps can then be used to determine the atomic potentials of the ions under consideration.

We have used these formalisms for the first time up to the sixth order. Furthermore, we could show that temperature factors based on the Gram-Charlier expansion work much more effectively than those based on the Edgeworth expansion, which has been used earlier for this type of structure investigation of fast ionic conductors. These calculations were carried out with the program system Prometheus, which allows the refinements of anharmonic temperature factors based on the above mentioned formalisms. (Zucker, Perenthaler, Kuhs, Bachmann, Schulz, J. Appl. Crystal., submitted)