05.X-1 LATTICE SUMS AND THE MADELUNG CONSTANT; EWALD IN AMERICA.

David H. Templeton, Department of Chemistry, University of California, Berkeley, CA 94720, USA.

The electrostatic energy, often expressed as the Madelung constant, is the dominant term in the binding energy of ionic crystals, and it is needed in many kinds of research. Its calculation as an infinite sum of 1/r potentials converges slowly at best and diverges unless careful conditions are placed on the sequence of terms. Ewald (Ann. Physik, 1921, 64, 253-287), in his study of optical fields in a periodic lattice of resonators, found a method which uses Gaussian charge distributions and two series which converge rapidly and absolutely, one in direct space and one in reciprocal space. Bertaut (J. phys. radium, 1952, 13, 499-505) simplified the method by introducing the Patterson function, showed how finite charge distributions can reduce it to a single absolutely convergent series in reciprocal space, and adapted it for sums of multipoles. The single series is particularly advantageous for complex structures because atomic coordinates appear only in structure factors, not in interatomic distances. Reluctance to use these methods has spawned a vast literature of direct-space methods valid for specific cases but awkward to generalize. Modern computers may reduce the need for rapid convergence, but not the need to avoid divergence or the insidious convergence to incorrect values. Ewald's method, developed at a time of laborious computation, retains its value today and is an object lesson in the importance of good algorithms for fast computers. Ewald continued to study waves in crystals throughout his life, but his greatest influence in later years was as editor, teacher, leader in ACA and IUCr, and inspiration for others. His influence, often anonymous or obscure, pervades the work of this time.

05.X-2 NONLINEAR OPTIC PROPERTIES, STRUCTURE AND PHASE TRANSITIONS IN FERROIC CRYSTALS.

By S. C. Abrahams, AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

The properties of nonlinear optic materials such as lithium niobate are of substantial technological significance in integrated optic devices. Among the most important nonlinear optic ferroics are ferroelectric crystals: these necessarily lack inversion centers and allow second-order interactions, may have both a relatively large nonlinear dielectric susceptibility and a large spontaneous birefringence, and may hence permit phase matching of fundamental to second harmonic waves. A major characteristic of ferroelectric crystals is the reversibility of polar axis sense by means of atomic displacements that may approach 1Å in amplitude. The crystallographic literature provides a rich source of atomic coordinates from which the presence of this characteristic may be inferred. New and potentially interesting ferroic crystals may thus be identified from structures determined for totally unrelated reasons. Several families of new nonlinear optic crystals have thereby been recognized: in each case the Curie temperature, at which the transition from ferroelectric to paraelectric phase takes place, that is predicted from the atomic displacements is in satisfactory agreement with experiment. For example, a value of T_c = 685K is predicted in $SrAlF_5$ and 695K is found by heat capacity measurement. Comparable phase transitions have been determined in eight isomorphous members of this family. The atomic arrangement in $Pb_5W_3O_9F_{11}$, archetype of an entirely new ferroic family, is considered in relation to properties such as nonlinear dielectric susceptibility, heat capacity, dielectric permittivity and dielectric loss that have been measured recently in several members of this and a related ferroic family.

05.X-3 DIFFUSE SCATTERING AND PHASE TRANSITIONS.

By H. Boysen, Institut für Kristallographie der Universität München, FRG.

Structural phase transitions are usually characterized by a change of symmetry of the average structure of the crystal, i.e. a change between two different states of (long range) order. It is well known that such transitions may be preceeded by localized diffuse scattering due to critical fluctuations and soft modes, which anticipate the new structure in space and time. There is not always a unique predetermination of the new phase to be realized below the transition temperature. E.g. in K_2SnCl_6 one observes a system of diffuse streaks from large librational motions of Cl_6-octahedra, which are strongly correlated in (100) planes, but are completely uncorrelated perpendicular to them. Close to the critical temperature antiphase librations dominate leading finally to an antiferroic ordering.

On the other hand, for a proper understanding of the microscopic mechanisms taking place at a phase transition it is important to consider also the deviations from the idealized average structures, which may undergo transitions as well. Such disorder phenomena are often intimately connected with the physical and chemical properties of the crystal. If structural subunits like chains or planes are involved, one observes in a diffraction experiment diffuse sheets and streaks, respectively. In urea inclusion compounds a number of such changes between two different states of disorder occur in successive phase transitions. These concern mainly the (translational and orientational) distribution of the guest molecules (e.g. paraffins) along channels formed by the urea host framework, but also interactions between guest and host, and finally a breaking into (longitudinal) domains of the whole crystal. In addition, a formation and vanishing of (lateral) domains at one of the transitions can be deduced from "wavy" streaks caused by internal interfaces.

It may also happen that a change of disorder alone occurs without a simultaneous transition of the average structure. In non-stoichiometric K-hollandite ($K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$) X-ray photographs at high temperatures show diffuse sheets perpendicular to c* at positions l = 0.23, 0.77, 1.54, 1.77,...., which can be interpreted by a short range order of the K^+ -ions being aligned along chains parallel to c. At low temperatures this turns into a rational system (l = n*0.2) indicating resonance with the (stable) framework. Thus one has - in a strict sense, i.e. when the crystal is regarded as a whole - an incommensurate - commensurate transition between two states of disorder (alternatively a one dimensional crystal).

In favourable cases it is possible to obtain information about the diffuse scattering at phase transitions also from powder patterns. They often provide a first hint on a possible influence of disorder and it is then usually very easy to follow its dependence on temperature. Moreover, if with neutrons integral and elastic diagrams are recorded simultaneously, one can determine its static or dynamic origin immediately. The phase transitions in quartz and leucite will serve as examples.

This work was supported by funds of the BMFT.