greater detail by powder neutron diffraction and the switching is shown to occur at very mild pressure at room temperature with a hysteresis of about 100 bar. The role of hydrogen bonding, lattice strain, and the pressure dependence of the EPR spectrum [3] will be discussed in light of these results.

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PS11.05.39 MOLECULAR REARRANGEMENTS IN TETRAMETHYLAMMONIUM TETRAFLUOROBORATE (TMT). Thomas M. Schultz, Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark, and Finn K. Larsen, Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

The thermal behaviour of tetraalkylammonium tetrafluoroborates includes series of phase transitions.[1] The present study is part of an attempt to characterize the molecular rearrangements over an extended temperature range in terms of constrained rigid body motion. TMT at room temperature crystallizes in a tetragonal space group, P4/nmm. The $(CH_3)_4N^+$ ions sit ordered at special positions (3/4, 1/4, 1/2) of point symmetry 42m, while the BF_4^- ions are placed at general positions near a 4mm axis. This imposes an eight-fold disorder on the BF_4^- ion. Furthermore, two equilibrium positions exist for each group. They are nearly related by a rotation of approximately 40 degrees around an axis near one of the BF bonds. A rigid body TLX refinement gives R(F) = 3.7% with 78% occupation for the major set. Lowering the temperature to 160 K, just above the phase transition at 154 K, depopulates the minor set completely, R(F) = 3.1 %.

The phase transition is accompanied by a doubling of unit cell volume and a change to monoclinic space group symmetry. Twinning is involved and most diffraction peaks split up at the phase transition. A twin model allowed to establish a fully ordered structure for data collected at 140 K.

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PS11.05.40 STRUCTURES AND PHASE TRANSITIONS OF HALOGENOMETALLATES(II) OF GERMANIUM AND TIN WITH MONOVALENT COUNTERCATION. B.R. Serr, G. Wittenburg, D.G. Ebling, H.W. Rotter and G. Thiele, Institut f. Anorg. & Analyt. Chemie und Materialforschungszentrum der Albert-Ludwigs-Universität, D-79104 Freiburg i. Br., Germany

Systematics of structures and phase transitions of the title compounds were studied by X-ray diffraction, Raman spectroscopy, DTA/DSC and impedance spectroscopy. A set of 45 structures at ordinary temperature and 27 high temperature or high pressure phases was used to study the effects of size and shape of the countercation (Rb, Cs, $MeNH_3$, Me_2NH_2, Me_3NH and Me_4N), the used halogen (Cl, Br or I) and above all to characterize and quantify the influence of the stereochemically active lone pair of divalent germanium and tin [1,2]. Besides other compositions, the main part of the title compounds crystallize in perovskite type structures AMX_3. Normally, M(II) is coordinated by a halogen octahedron. While regular coordination is found among the tin compounds, the environment of Ge(II) is always [3+3] distorted, due to the effect of the lone pair. Raman spectroscopy shows, that Ge(II) and Sn(II) are disordered in the hexagonal packed structures of AMI_3 with A= Me_4N, while they are fixed for A = Me_2NH_2. Many of the studied compounds are polymorphous and transform to the cubic modification at elevated temperatures. The studied phase transitions show reconstructive or dilatative / displacive mechanisms, the HT-phases are strongly disordered due to cation libration and disordering of M(II) in its X_6-octahedron. The transitions are accompanied by drastic changes of the dielectric properties. The characterisation of the thermal behaviour proofs impedance spectroscopy as a splended tool for the examination of phase transitions.

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PS11.05.41 PRESSURE-INDUCED MODULATED PHASES OF $[N(CH_3)_4]_2CuCl_4$. S. Shimomura, N. Hamaya[1], Y. Fujii[2], T. Fukui, H. Terauchi, Department of Physics, Kwansei-Gakuin University, Nishinomiya, Hyogo 662, Japan, [1]Department of Physics, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan, [2]Neutron Scattering Laboratory, Institute for Solid State Physics, The University of Tokyo, Shirakata, Tokai, Ibaraki 319-11, Japan

The A_2BX_4 type dielectrics are known to have various commensurate (C) and incommensurate (IC) phases. Tetramethylammonium tetrachlorocuprate $[N(CH_3)_4]_2CuCl_4$, which belongs to the A_2BX_4 type, undergoes the successive phase transitions with decreasing temperature from the prototypical normal (N) phase to the IC phase at 26°C and to the C phase characterized by $q = c^*/3$ at 19°C. We carried out x-ray diffraction measurements under hydrostatic pressure using a beryllium-cylinder pressure cell and a diamond-anvil cell in order to determine the pressure and temperature dependence of the modulation wave vector and to explore additional pressure-induced phases.

The IC phase characterized by $q < c^*/3$ decreases its stable range with increasing pressure and finally vanishes at a point (23.4MPa, 30.0°C), which is denoted by L*. Another IC region characterized by $q > c^*/3$ is found to appear at L* and widen with increasing pressure. The second-order N-IC phase line and the first-order IC-C phase line meet at L*, where the phase transition between the N and C phases is considered to take place directly. The modulation wave vector in both IC regions tends to $c^*/3$ monotonically as the L* point is approached. These facts suggest that the L* point is a multicritical one in incommensurate systems. Applying higher pressure at room temperature, we found the existence of three more phases up to about 4 GPa.

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PS11.05.42 LOW-FREQUENCY DIELECTRIC DISPERSION AND PYROEFFECT AT PHASE TRANSITION FOR MONOCLYNIC TELLURIUM ACID AMMONIUM PHOSPHATE CRYSTAL. I.A.Smirnova, N.N.Bolshakova*, N.D.Gavrilova Moscow State University, Moscow, Russia, *Tver State University, Tver, Russia

In this paper temperature dependencies of pyroelectrical effect and low-frequency dielectrical dispersion of monoclinic Tellurium Acid Ammonium Phosphate crystal (TAAP) $Te(OH)_2*2NH_4H_2PO_4*(NH4)_2HPO_4$ (Tc=318K) in frequency range 20Hz-10kHz and temperature region 220-320K were investigated. Temperature dependence of pyrocoefficient is unusial for ferroelectric crystals - the peak has a 40K shift to ferroelectric phase and has a diffuse shape. We connect it with the turn of crystal cell total dipole moment, in which, probably, hydrogen bonds play important role. Dielectric dispersion data were used to

test the "universal law" of dielectric response; parameters n and m were estimated.

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PS11.05.43 NEUTRON DIFFRACTION STUDY OF THE MARTENSITIC PHASE TRANSFORMATION IN In-Tl ALLOYS.

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InTl binary solid solutions with Tl concentrations between 15.5 and 31.0 atomic percent are know to undergo a martensitic phase transition from face-centered cubic, fcc, to face centered tetragonal, fct, upon cooling below the transformation temperature, Tm. Tm depends strongly on the Tl concentration dropping from 425K at 15.5 atomic percent Tl to nearly zero Kelvins at 31.0 atomic percent Tl. Appreciable phonon softening has been predicted from the theoretical calculation of the phonon dispersion relations and because the elastic stiffness modulus, $c' = (c11 - c12)/2$, approaches zero near Tm. A careful measurement of the phonon dispersion curves using inelastic neutron scattering, however, shows no phonon softening within the accessible Q range, but rather a slight hardening as would be expected for a metal. The discrepancy between the temperature dependence of c' and the complicated behavior of the phonon dispersion has yet to be resolved.

The intent of the present study is to examine more closely the structural changes that take place when the alloy transforms. High resolution neutron diffraction patterns were collected at several temperatures starting at 300K and decreasing to 9K on a In(23at%)Tl(77at%) polycrystalline sample. The martensitic transformation is observed to begin around 250K when the peaks associated with the face-centered cubic phase develop small shoulders. The structure continued to change continuously as the temperature was decreased even though the sample had completely transformed to the fct phase at around 200K. Upon warming the fcc phase reappeared 15K above where it vanished when cooling and the lattice parameters showed very little histeriesis. The sample had completely transformed back into the fcc phase by 260K. From these results we conclude that this martensitic transformation is weakly first order in the sense that the c/a ratio on the fct phase continues to increase as the temperature is lowered all the way down to 9K. It is important to remember, however, that this is a polycrystalline sample and any strains present could have a large affect on these observations. Further single crystal work is necessary in order to determine with more certainty the details of this transformation.

PS11.05.44 RAMAN SPECTRA INVESTIGATION OF TEMPERATURE PHASE TRANSITIONS IN ALKALI METAL PERCHLORATES.

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It was discribed the obtained Raman spectra for wide temperature region (at room temperature to metling one). The degeneration of internal moleculer frequences is increased with growth of temperature and differ from as room - temperature data so ones predicted by symmetrical analysis. For example the Y2 mode of LiClO4 contains two line for both solid phases. This fact indicates the higher temperature phase has a noncubic distorsion. For (K, Rb, Cs)ClO4 the Y1 mode consist of only one line. The other mode (Y3) contains two lines for low teperature state which go out after phase transition. Such behaviour does not coincide with generally admitted interpretation of nature of these frequencies. On the base of the obtained data it was proposed the new interpretation main modes (Y1, Y2, Y3) and elobarated the teoretical model explaining in frame work of slow symmetry the temperature behaviour of Raman spectra. This model connects the significances of frequance splittiny with the temperature structure distorsin. In particuler the higher phase is pseudocubic (the tetragonal type) for NaClO4 and it is cubic for (K, Rb, Cs)ClO4. The last have tetragonal low temperature phase turning into ortorombic one under the room temperature.

PS11.05.45 AMMONIUM FLUOROBERYLLATE; NEUTRON STRUCTURE IN TWO PHASES.

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Ammonium fluoroberyllate [$(NH_4)_2BeF_4$] undergoes a ferroelectric transition at 175 K (Pepinsky & Jona, Phys. Rev., 1957, 105, 344-345) and a non-ferroelectric transition at 182 K (Makita & Yamauchi, Phys. Soc. Jpn., 1974, 37, 1470). The phases are orthorhombic. The ferroelectric phase has a superlattice with the superlattice a-axis double that of the room-temperature phase. The intermediate phase also has a similar superlattice but is incommensurate along the a-axis (Iizumi & Gesi, Solid State Comm., 1977, 22, 37). The room-temperature x-ray structure has been reported by Garg & Srivastava (Acta Cryst., 1979, 335, 1432) and the ferroelectric phase x-ray structure by Srivastava & Craven (abstract PJ23, ACA Annual Meeting, 1991).

To obtain more accurate hydrogen positions the crystal structures at 200 K, 163 K and 20 K have been determined from neutron diffraction. The slight tilts of BeF_4^- and NH_4^+ ions from the mirror planes present in the paraelectric phase result in stronger hydrogen bonds in the ferroelectric phase. Two NH_4^+ ions reorient parallel to the polar b-axis. These will have some dipole moment and appear to be primarily responsible for ferroelectricity in the low temperature phase. Details of the neutron diffraction results will be presented.

PS11.05.46 THE STRUCTURE OF $Cs_5(HSO_4)_3(H_2PO_4)_2$.

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The new compound $Cs_5(HSO_4)_3(H_2PO_4)_2$ was synthesized as part of an ongoing study to examine the relationship between hydrogen bonding and phase transitions in solid acid compounds. The compound crystallizes in space group C2/c and has lattice constants a = 34.07(2), b = 7.661(4), c = 9.158(6) Å and b = 90.44(2)°. The structure of $Cs_5(HSO_4)_3(H_2PO_4)_2$ contains both layers and chains of hydrogen-bonded XO_4 groups (where X = P or S). Phosphate groups form corrugated layers that are perpendicular to b, whereas sulfate groups form branched chains, located between the phosphate layers. These chains extend along c. The compound is unusual in that the two crystallographically distinct SO_4 sites have different numbers of hydrogen-bonded oxygen atoms: S(1) has only one oxygen nearest neighbor that is hydrogen bonded whereas all 4 oxygen atoms bonded to S(2) are additionally hydrogen-bonded to neighboring oxygen atoms. Similarly, all oxygen atoms participating the PO_4 tetrahedra are hydrogen bonded.

The presence of both hydrogen-bonded and non-hydrogen-bonded oxygen atoms suggests that the material will undergo a superprotonic phase transition at elevated temperatures. Indeed, a transition is observed at 391K by differential scanning calorimetry. Furthermore, the presence of locally disordered hydrogen bonds suggest the material will undergo a ferroelectric material at low temperatures.