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.


PS11.05.39 MOLECULAR REARRANGEMENTS IN TETRAMETHYLMAMMONIUM 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 tetramethylammonium tetrafluoroborates includes series of phase transitions. The present study is part of an effort 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/mnm. The (CH₃)₄N⁺ ions sit ordered at special positions (3/4, 1/4, 1/2) of point symmetry 42m, while the BF₄⁻ ions are placed at general positions near a 4mm axis. This imposes an eight-fold disorder on the BF₄⁻ 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.

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.


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 counterion (Rb, Cs, MeNH₃, Me₂NH₂, Me₃NH and Me₄N) and the used halogen (Cl, Br or I) and above all to characterize and quantify the influence of the stereochemically active lone pair of the used halogen atom. The environment of Ge(II) is always [3+3] distorted, while the environment of Sn(II) is always [3+5] distorted, due to the effect of the lone pair.

Many of the studied compounds are polymorphous and transform to the cubic modification at elevated temperatures. The studied phase transitions show reconstructive or dilative / displacive mechanisms, the HT-phases are strongly disordered due to cation libration and disordering of M(II) in its X₅-octahedron. The transitions are accompanied by drastic changes of the dielectric properties. The characterisation of the thermal behaviour proofs impedance spectroscopy as a splendid tool for the examination of phase transitions.


PS11.05.41 PRESSURE-INDUCED MODULATED PHASES OF [N(CH₃)₄]₂CuCl₄. Sh. Shimomura, N. Hamaya¹, Y. Fujii², T. Fukui, H. Terauchi, Department of Physics, Kwansei-Gakuin University, Nishinomiya, Hyogo 662, Japan, ¹Department of Physics, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan, ²Neutron Scattering Laboratory, Institute for Solid State Physics, The University of Tokyo, Shiharakata, Tokai, Ibaraki 319-11, Japan

The A₂BX₄ type dielectrics are known to have various commensurate (C) and incommensurate (IC) phases. Tetramethylammonium tetrachlorocuprate [N(CH₃)₄]₂CuCl₄, which belongs to the A₂BX₄ 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 berillium-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 point 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 MONOCLINIC TELLURIUM ACID AMMONIUM PHOSPHATE CRYSTAL. I.A. Smirnova, N.N. Bolshakova, N.D. Gavrillova Moscow State University, Moscow, Russia; Tver State University, Tver, Russia

In this paper temperature dependences of pyroelectrical effect and low-frequency dielectric dispersion of monoclinic Tellurium Acid Ammonium Phosphate crystal (TAAP) Te(OH)₂·2NH₂H₂PO₄·(NH₄)2HPO₄ (Te=181K) in frequency range 20Hz-10kHz and temperature region 220-320K were investigated. Temperature dependence of pyrocoefficient is unusual 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.


**PS11.0543 NEUTRON DIFFRACTION STUDY OF THE MARTENSITIC PHASE TRANSFORMATION IN In-Ti ALLOYS.** H.G. Smith and J.L. Robertson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA, T. R. Finlayson, Monash University, Clayton, Australia M. Wuttig, University of Maryland, College Park, Maryland, USA

InTi binary solid solutions with Ti concentrations between 15.5 and 31.0 atomic percent are known 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 Ti concentration dropping from 425K at 15.5 atomic percent Ti to nearly zero Kelvins at 31.0 atomic percent Ti. Appreciable phonon softening has been predicted from the theoretical calculation of the phonon dispersion relations and because the elastic stiffness modulus, \( c' = (c_{11} - c_{12}/2 \) 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(2at%)/Ti(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 hysteresis. 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.

**PS11.0544 RAMAN SPECTRA INVESTIGATION OF TEMPERATURE PHASE TRANSITIONS IN ALKALI METAL PERCHLORATES.** V.I. Snejkov, North Caucasus Scientific Center, 140, Pushkinskaya, Rostov-on-Don, 344006, Russia

It was described the obtained Raman spectra for wide temperature region (at room temperature to melting one). The degeneration of internal molecular frequencies 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 monoclinic distorsion. For (K, Rb, Cs)ClO4 the Y1 mode consist of only one line. The other mode (Y3) contains two lines for low temperature 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 elaborated the theoretical model explaining in frame work of slow symmetry the temperature behaviour of Raman spectra. This model connects the significances of frequency splitinity with the temperature structure distortin. In particular the higher phase is pseudocubic (the tetragonal type) for NaClO4 and it is cubic for (K, Rb, Cs)ClO4. The fast have tetragonal low temperature phase turning into ortorombic one under the room temperature.

**PS11.0545 AMMONIUM FLUOROBERRYLLATE; NEUTRON STRUCTURE IN TWO PHASES.** By R. C. Srivastava*, Department of Physics, Indian Institute of Technology, Kanpur 208016, India; W. T. Klooster and T. F. Koetzle, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

Ammonium fluoroberryllate \((NH_4)_2BeF_4\) 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 Crystal., 1979, 355, 142) and the ferroelectric phase x-ray structure by Srivastava & Craven (abstract P23, 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 shifts of BeF_4^2- and NH_4^+ ions from the mirror planes present in the paraelectric phase result in stronger hydrogen bonds in the ferroelectric phase. Two NFL^+ 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.

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**PS11.0546 THE STRUCTURE OF \(Cs_5(\text{HSO}_4)_{12}(\text{H}_3\text{PO}_4)_2\).** G. Stareff, P. Calkins, S. Fu and S.M. Haile, Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195

The new compound \(Cs_5(\text{HSO}_4)_{12}(\text{H}_3\text{PO}_4)_2\) 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 \(a = 34.07(2), b = 7.661(4), c = 15.9(1)\), and \(\beta = 90.44(2)\). The structure of \(Cs_5(\text{HSO}_4)_{12}(\text{H}_3\text{PO}_4)_2\) contains both layers and chains of hydrogen-bonded \(\text{SO}_4\) 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 \(\text{SO}_4\) 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 \(\text{PO}_4\) 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.