

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.

1. B. J. Hathaway and A. W. Hewat, *J. Solid State Chem.* **51**, 364 (1984).
2. C. J. Simmons, M. A. Hitchman, H. Stratemeier and A. J. Schultz, *J. Am. Chem. Soc.* **115**, 11304 (1993).
3. W. Rauw, H. Ahsbahs, M. A. Hitchman, S. Lukin, D. Reinen, A. J. Schultz, C. J. Simmons and H. Stratemeier, *Inorg. Chem.*, in press (1996).

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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 (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. 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.

1. Zabinska, G., Ferloni, P. and Sanesi, M. *Thermochimica Acta* **122** (1987) 87-94.

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 counterion (Rb, Cs, MeNH₃, Me₂NH₂, Me₃NH and Me₄N), 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 AMX₃. 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 AMI₃ with A = Me₄N, while they are fixed for A = Me₂NH₂. 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 X₆-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.

- [1] B.R. Serr, G. Heckert, D.G. Ebling, H.W. Rotter and G. Thiele, *J. Mol. Struct.* **348** (1995) 95-98.
- [2] U. Schwarz, H. Hillebrecht, M. Kaupp, K. Syassen, H.G. v. Schnering and G. Thiele, *J. Solid State Chem.* **118** (1995) 20-27.

PS11.05.41 PRESSURE-INDUCED MODULATED PHASES OF [N(CH₃)₄]₂CuCl₄. S. Shimomura, N. Hamaya¹⁾, Y. Fujii²⁾, T. Fukui, H. Terauchi, Department of Physics, Kwansai-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 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 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 MONOCLINIC 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*2NH₄H₂PO₄*(NH₄)₂HPO₄ (Tc=318K) 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