05.1–56 MICROCRYSTALLOGRAPHIC CALORIMETRY: THERMOTROPIC LIPID PHASE TRANSITIONS CHARACTERIZED *VIA* ELECTRON DIFFRACTION. By Douglas L. Dorset, Electron Diffraction Dept., Medical Foundation of Buffalo, Inc., 73 High St., Buffalo, NY 14203, U.S.A.

Although temperature-controlled sample holders for electron microscopes have been available since the 1930's for the study of organic materials, they have not been frequently employed for a quantitative crystallographic study of polymorphism. Many biological lipids exhibit such polymorphism which is responsible for their functional behavior. Since such compounds are most conveniently prepared as thin microcrystals (either by solution- or epitaxial-growth), they are readily studied by electron diffraction. The oblong shape of these molecules defines the axial projection length obtained by each crystal growth technique and, given inevitable elastic crystal bends, this length determines what structural information can be derived from the electron diffraction intensities (Dorset, Ultramicroscopy (1983) 12, 19-28; Moss and Dorset, Acta Cryst. (1983) A39, 609-615). Experimental structure determination on alkyl chain substances demonstrate this point, i.e. only methylene "subcell" packing is evident from the electron diffraction data from solution-grown crystals (long unit cell projection but short subcell projection) whereas a total structure analysis is obtained with epitaxially-grown crystals (short unit cell projection).

Heating these microcrystals in the electron microscope (e.g. GATAN model 626 cryotransfer specimen holder with temperature range -170°C to 150°C) allows one to follow their thermotropic phase behavior as illustrated by three examples:

(1) Electron diffraction data (hk0) from solution-grown crystals of normal even chain paraffins clearly reveal the transition from the orthorhombic to the hexagonal pre-melt form. Data (0kℓ) from crystals epitaxially-grown on benzoic acid allow one to distinguish among several suggested chain melting models: reduced resolution of lamellar 00ℓ reflections but relative invariance of strong 0kℓ intensities due to the Fourier transform of the chain zig-zag are in accordance with a kinked chain model which includes chain end voids.

(2) Microcrystals of di(n-C_{16} radyl) phosphatidylethanolamines epitaxially crystallized on naphthalene indicate that both the ester- and ether-linked compounds give basically the same smectic liquid crystal form. Some difference in the melting temperatures of chiral and racemic dipalmitoyl compounds was also found.

(3) Solution-grown microcrystals of cholesteryl myristate reveal the 71°C transition of the crystal form to the smectic mesophase (diffuse ring at 5.3Å) as shown by Price and Wendorff (J. Phys. Chem., 75, (1971) 2839-2849). Large area crystals (≥10μm diam.) are obtained by cooling the smectic phase but cooling from the cholesteric phase (>80°C) through the smectic produces spherulitic crystals. A previously uncharacterized crystal form exists (at least) below -145°C with the shortest unit cell spacings double the room temperature form (a=20.84±0.12Å b=15.36±0.12Å c/2=50.58±0.39Å). Streaking along the a^* direction may indicate a "cigarello" packing of alternately oriented laths with nearly equivalent polar crystal structures. Transition from the crystalline bilayer to the smectic mesophase is also observed with epitaxially-crystallized samples, giving a sharp diffraction doublet at 33.66±0.45Å oriented in the same direction as the crystal phase 00ℓ reciprocal lattice row.

Research supported by NIH grant GM21047.

05.1–57 THE STRUCTURE AND SUCCESSIVE PHASE TRANSITION IN CHOLESTERYL 2,2,3,3-TETRAFLUOROPROPIONATE (CTFP). By Y. Yoshimura, N. Nakamura and K. Shimaoka, Faculty of Science and Engineering, Ritsumeikan University, Kyoto, Japan. and S. Yano, Faculty of Engineering, Gifu University, Gifu, Japan.

CTFP single crystals undergo phase transitions at 178, 143 and 123K, and at the phases below 178K, the samples show various modulated structures along b direction (Nakamura et al., J. Appl. Crystallogr. in press). A crystal structure at room temperature is monoclinic, either $P2_1$ or $P2_1/m$ with a=12.44(1), b=9.27(1), c=13.30(1)Å and β=106.0(1)°, and contains two molecules in the unit cell. Below 123K, the modulated lattice constant along b-axis is 5 times as long as b, although the symmetry is the same as that of room temperature. The present work is to make clear a mechanism of the appearance of the modulated structures in the lower temperature phases. Experiments were performed by taking X-ray precession and Laue photographs at temperatures down to 85K. In consideration of an aspect of the molecular configuration, the modulated structures are explained by phase modulation arising from sinusoidal distortions. The displacements of CTFP molecules have a component along the unique axis of the crystal. On the other hand, one dimentional diffuse scatterings originated in the modulated structure are observed on the c*-planes at 85K. These scatterings leave the traces even if the temperature rises above 178K. This fact indicates a presence of another mode of displacement by phase transitions.

05.1–58 ANOMALOUS PRESSURE DEPENDENCE OF ELASTIC PROPERTIES OF ALPHA ALUMS. By S. Haussühl, A. Kranzmann and R. Podeswa, Institut für Kristallographie zu Köln, Zülpicherstr. 49, 5000 Köln 1, FRG.

Most ammonium and selenate alums of the alpha type exhibit a significant nonlinear pressure dependence of the elastic constants c_{11} and c_{12} within a small pressure range between 0 and 4 kbar ($d^2c_{11}/dp^2, d^2c_{12}/dp^2 > 0$). At higher pressures a tendency towards a normal linear pressure dependence is observed. dc_{44}/dp and $d(c_{11}-c_{12})/dp$ are quasi-constant in the whole range of measurements up to 7 kbar. Therefore the symmetry type of interaction involved in these anomalies is a totally symmetric one, represented by the bulk compressibility K. In certain cases like $NH_4Al(SO_4)_2\cdot 12H_2O$ and $KAl(SeO_4)_2\cdot 12H_2O$ the values dc_{11}/dp decrease strongly with decreasing temperature, resulting in negative values of dK^{-1}/dp, a quantity which usually shows values of ca 5 in all stable crystals. In the series of selenate alums with different monovalent cations the anomalies are less pronounced the larger the monovalent ion is. Other alums, especially all beta alums, exhibit no such anomalies.

All alums, for which recent structure analyses have revealed the existence of different equilibrium positions of the NH_4- and SeO_4-tetrahedra, show the described anomalies. We therefore suggest that the anomalies are a consequence of a pressure induced redistribution of the occupancies of such lattice sites. In the case of ammonium alums the anomalous temperature dependency of the pressure derivatives dK^{-1}/dp is apparently related to the known phase transitions at low temperatures.