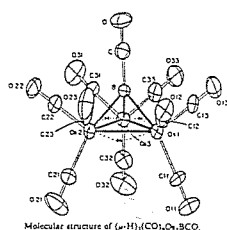


05.2-24 CRYSTAL AND ELECTRONIC STRUCTURE OF $(\mu\text{-H})_3(\text{CO})_9\text{Os}_3\text{BCO}$. By Leh-Yeh Hsu, Deng-Yang Jan and Sheldon G. Shore, Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

The title compound (I) has been prepared and characterized by single-crystal X-ray diffraction as well as spectroscopic methods (^{13}C , ^{11}B , and ^1H NMR). The compound is a carbonyl borylidyne capped Os_3 triangle as shown in the figure.



The electronic structure of I has also been studied by using the Fenske-Hall quantum chemical approach with a fragment analysis in terms of the metal cluster $\text{H}_3(\text{CO})_9\text{Os}_3^+$ and capped ligand BCO. The calculation suggests that the apical boron is electron rich and the π system acts as an electron donor and electron acceptor. A localized MO description with a sp-hybridized boron forms a dative bond to the metal triangle and the remaining p orbitals form multi-centered π bonds to the Os_3 cluster.

The BCO unit in I has $\text{B-C}=1.469(15)\text{\AA}$ and $\text{C-O}=1.145(15)\text{\AA}$, while in H_3BCO (II) has $\text{B-C}=1.54\text{\AA}$ and $\text{C-O}=1.31\text{\AA}$. The CO stretching frequency is 2120 cm^{-1} in I and 2140 cm^{-1} in II. To explain this difference, nonparameterized Fenske-Hall molecular orbital calculations are carried out on both I and II with a fragment analysis in terms of $\text{H}_3(\text{CO})_9\text{Os}_3\text{B}$ and CO for the former, H_3B and CO for the latter. The calculation suggests that the back π bonding in I is more significant, due to the predominant movement of the electron density of the main Os_3B bonding orbitals to the CO π anti-bonding orbitals.

05.2-25 THE EFFECT OF CRYSTAL STRUCTURE AND PHASE STABILITY ON THE SUPERCONDUCTIVITY OF EQUIATOMIC TERNARY PNICTIDE COMPOUNDS* By G. P. Meisner, Los Alamos National Laboratory, MST-5, Los Alamos, NM 87545, USA.

The equiatomic ternary compounds $\text{MM}'\text{X}$ with $\text{M} = \text{Ti}$, Zr , or Hf , $\text{M}' = \text{Ru}$ or Os , and $\text{X} = \text{P}$ or As typically crystallize at high temperatures in the ZrRuSi -type hexagonal structure (P62m , M in 3(g), M' in 3(f), and X in 2(c) and 1(b)) and exhibit superconductivity at temperatures as high as 13.3 K for ZrRuP (Barz, Ku, Meisner, Fisk, and Matthias, Proc. Natl. Acad. Sci. USA (1980) 77, 3132; Meisner, Ku, and Barz, Mater. Res. Bull. (1983) 18, 983). These compounds are metastable and crystallize at low temperature in the TiNiSi -type or TiFeSi -type orthorhombic structures with $\text{X} = \text{P}$ or As , respectively. These three structures are all built from essentially the same crystal subunits. The TiNiSi -type structure (Shoemaker and Shoemaker, Acta Crystallogr. (1965) 18, 900) arises from a substantial re-arrangement of the subunits compared to the hexagonal structure yet superconductivity persists at the moderate temperature of 3.9 K for orthorhombic ZrRuP (Meisner and Ku, Appl. Phys. (1983) A31, 201). The TiFeSi -type structure is a superstructure of the hexagonal phase with very nearly the same arrangement of atoms (Jeitschko, Acta Crystallogr. (1970) B26, 815) but results in the disappearance of superconductivity in HfRuAs (Meisner, Phys. Lett. (1983) 96A, 483). The occurrence of the TiFeSi -type superstructure among the $\text{MM}'\text{X}$ ternary compounds with $\text{X} = \text{P}$, As , Si , or Ge correlates with Fe or Ru occupying the hexagonal 3(f) site and consequently the underlying distortion can be rationalized as a sharing of unpaired electrons between pairs of Fe or Ru atoms. The nature of the distortion suggests superconductivity originates with the $\text{M-M}'$ zig-zag chains which are present and undistorted in both superconducting modifications of ZrRuP but are distorted in the non-superconducting modification of HfRuAs .

*This work supported by US DOE.

05.2-26 A COMPARISON OF THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE POLYMORPHS OF NEMATOGENIC 4,4'-BIS-(ETHOXY)AZOXYBENZENE. By C. E. Pfluger, Dept. of Chem., Syracuse University, Syracuse, N.Y., and R. D. Gilardi, and C. F. George, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C., USA.

The room temperature structures (22°C) of three crystal polymorphs of the compound 4,4'-bis(ethoxy)-azoxybenzene (also called p,p'-azoxydiphenetole), a compound exhibiting a nematic liquid crystalline phase from 137 to 168°C , as well as a low-temperature structure of the triclinic polymorph, have been determined. These structures represent the initial phase of a systematic variable temperature X-ray crystallographic study of several members of a homologous series (4,4'-bis(methoxy)-, 4,4'-bis(ethoxy)-, and 4,4'-bis(propoxy)-azoxybenzene) in an attempt to obtain information regarding the intra- and inter-molecular interactions which must account for the liquid crystalline behavior of this series of compounds. The isolation of three crystal polymorphs at room temperature presents an opportunity to compare the intra- and inter-molecular interactions for this nematogenic molecule in three different packing arrangements. A comparison of the low- and room-temperature structures has been useful in extracting atomic thermal motion information from the somewhat disordered crystal structure of the triclinic polymorph.

05.2-27

The study by electron microscopy of virgin crystals (Franco and Fernández-Ferrer, 1984) obtained by evaporation from a water solution, shows two kind of crystals, which we have identified by X-ray powder analysis; 46 relevant peaks of diagramme are indexed according to the cell parameters of structure of ferroelectric phase of TGS, and 41 with the cell parameters of switching fatigued structure.

The appearance of pyroelectric phase of TGS in the virgin crystals suggest the possibility to remove a crystal and refine, the previous crystal structure, because switching fatigued crystals show a lot of defects due to the aging process. The virgin pyroelectric phase has crystals with $a=9.190(6)$, $b=12.662(3)$, $c=5.751(7)$ $\beta=105.7(7)^\circ$ and refinement leads to $R=0.026$ ($R_w=0.033$).

In order to determine the different morphology of crystals, a study by Hartmann-Peardock theory has been carried out. A first result has been that the crystallization energy of ferroelectric phase is less than pyroelectric one. This suggest to use a method of crystallization in which the pyroelectric phase would not be obtained. Experimental results show that pyroelectric phase does not growth in low supersaturation, while it is obtained to higher values of supersaturation.

STUDY ON CRYSTAL STRUCTURE AND GROWTH OF PYROELECTRIC

PHASE OF TRIGLYCINE SULPHATE. By X. Solans, M. Font-Altaba C. Miravittles and M. Aguiló. Dept. de Cristallografia, Univ. Barcelona, Granvia 585, (Barcelona-11); Instituto Jaime Almera, CSIC-Barcelona, and Facultat de Química, Tarragona.

Franco et al. has shown the inhibition of ferroelectric switching, when TGS crystals are treated during 1000 hours with an electric potential. In order to determine whether the inhibition may be explained in terms of the structure, we have determined the crystal structure of a switching fatigued crystal. The results obtained are:

$C_6H_{17}N_3O_{10}S$. Monoclinic, $P2_1$, $a=9.152(2)$, $b=12.640(2)$, $c=5.768(1)$, $\beta=105.5(2)^\circ$, $Z=2$. The structure was solved by direct methods with the MULTAN system of computer programs and refined by full-matrix least squares. R final 0.066 (Rw=0.072).

The main difference among the crystal structure of the virgin TGS and the switching fatigued, are the cell parameters. The glycine I is twisted about 180° around the a-axis and 44.8° around the b-axis with respect to the position of these groups in the virgin crystal, and the sulphate ion is twisted only 44.8° around the b-axis; these rotations produce a non-simple movement in glycine II and III.

05.2-28 ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF PURE AND DOPED TRIGLYCINE SULPHATE SINGLE CRYSTALS. By M. Gaffar and A. Abu El-Fadi Physics Department, Faculty of Science, Assiut University, Assiut, Egypt.

The dielectric constant and both the A.C. and D.C. electrical conductivity of pure and doped single crystals of TGS are investigated in the temperature range 300-450°K. The influence of Ni, Cu, Co, Cr and Fe ions on the type of conduction, type of transition, transition temperature, Curie Weiss constants and the dielectric constant are studied. The effect of sample thickness and pressure contact on the electrical conductivity is also discussed. Some interesting features of the correlation between the valency and ionic radii of the dopant is presented.

05.2-29 GROWTH AND PROPERTIES OF FERROELECTRIC SINGLE CRYSTALS OF TETRAGONAL TUNGSTEN BRONZE STRUCTURE TYPE. By Ju. I. Kopylov, V. B. Kraychenko, A. T. Sobolev, Institute of Radio-engineering and Electronics, Academy of Sciences of the USSR, K. Marx av. 18, Moscow, GSP-3, 103907, USSR.

Crystal-chemical stability analysis is made for tetragonal tungsten-bronze structure type $A_4A_2C_4B_8B_2O_{30}$ (where \bar{A} and \bar{A}' are large cations in five- and four-sided channels of the structure, C are cations in three-sided channels, \bar{B} and \bar{B}' are multi-valent cations in two types of octahedra) in case when A are cations of alkaline and alkaline-earth metals. Single crystals of some solid solutions of this type are grown. The stability field of ferroelectric crystals having this structure type is determined for (Ba, Sr, Ca)Nb₂O₆ system. This field is shown to be much broader than for ceramic samples studied earlier (G. A. Smolensky et al., Fizika tverdogo tela, Moscow-Leningrad, 1959, v. 2, p. 244). Dielectric, optical and electrooptical properties of (Ba, Sr, Ca)Nb₂O₆ single crystals are studied.

Curie temperatures and half-wave voltage values increase and dielectric constant at room temperature ϵ'_c , widths of $\epsilon'_c(T)$ maxima and extent of broadening of ferroelectric phase transition decrease with increasing Ba contents in the crystals. Line widths of Gd³⁺ ESR spectra in the crystals increase with increasing of phase transition broadening. Structural reasons of this are given.

05.2-30 RELATIONS BETWEEN THE STRUCTURE, MORPHOLOGY AND PHYSICAL PROPERTIES OF TRIGONAL AND MONOCLINIC TRAl₃[BO₃]₄ CRYSTALS. L. I. Leonyuk and N. I. Leonyuk, Department of Geology, Moscow State University, Moscow, USSR.

Two structural types of TRAl₃[BO₃]₄ crystals are known. The one, possessing a R32 space group (structural type of huntite) is more stable. It exists in the entire series of rare-earth-aluminium orthoborates. At temperatures exceeding 1270 K, TR-Pr-Eu compounds are crystallized according to the C 2/c space group as well. There is a direct relationship between the development of hkl faces and the experimentally observed total intensity of X-rays reflected from the corresponding atomic lattices (e.g. I₀₀₁+I₀₀₂+I₀₀₃+...+I_{00l}). Faces {110}, {110} and {010} of monoclinic crystals correspond to two trigonal prisms {1120} and {2110} in huntite-structured crystals. The base-pinacoid {001} conforms to that having the same index in the trigonal crystal. The huntite rhombohedron {1011} of the monoclinic crystal is represented by a rhombic prism {111} and pinacoid {202}. The violated significance of the faces in monoclinic crystals as compared with the trigonal ones is due to the peculiarities of their internal structure. TRAl₃[BO₃]₄ crystals possess piezoelectric and nonlinear-optical properties. These properties vanish in the phase transition into the monoclinic modification.