

PS02.01.13 TROUBLESOME PERCHLORATES. Rita Gronbaek Hazell and Alan Hazell, Dept of Chemistry, University of Aarhus, DK8000 Århus C, Denmark.

Complexes of transition metals are often crystallized as the perchlorate salts, as these usually gives good crystals. Crystallographers are rarely impressed as experience tells us that these anions are often disordered to some degree. Over the years we have developed and adapted the following routines to facilitate work on disordered groups:

1. Fourier synthesis calculated on a sphere of desired radius around an atom, to get some idea as to how (dis)ordered the group is.
2. A freely rotating group can be treated by giving the chlorine atom a scattering factor calculated as: $f_{rot}(s) = f_{Cl}(s) + 4f_O(s)\sin(4\pi rs)/(4\pi rs)$
3. Disorder between 2 or more distinct orientations is dealt with by constraint refinement according to Pawley (1971) using the symmetric/identical molecule constraints and restricting the occupations to add up to 1.0.
4. Thermal motion is dealt with in the TLS or more usually TLX model to save parameters.
5. Large thermal motion together with geometric constraints requires that the TLS model is expanded to include third cumulants (Prince and Finger, 1973).
6. The case of a group rotating freely about a particular direction can be dealt with by means of a zero order Bessel function (Zachariassen, 1945)

The routines are quite general and care is taken to ensure that standard deviations of derived as well as refined parameters are calculated. The computer programs used at Århus stem from SUNY Buffalo and include modified ORFLS, ORFFE and FORDAP. Locally we have a menu driven system to run standard calculations with a minimum of effort. Work is still going on trying to make in particular the constraint refinement more user-friendly. For special needs the user will however still have to read the manuals. Some of the procedures described here may be adapted into other systems without too much trouble.

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E. Prince and L.W. Finger, Acta Cryst. (1973). B29, 179.

W.H. Zachariassen, Theory of X-Ray Diffraction in Crystals. (1945) 222.

PS02.01.14 A MULTIPLE WAVELENGTH STRUCTURE ANALYSIS OF $KTaO_3$. H.-G. Krane¹, A. Kirfel¹, K. F. Fischer², ¹Institut für Mineralogie, University of Würzburg, ²FR Kristallographie, University of Saarbrücken, Germany

Synchrotron radiation provides the opportunity to vary the radiation energy over a considerable range and thus to assess the reliability of structure parameters derived from least-squares refinements and to study the influence of absorption and extinction, particularly on the thermal displacement parameters.

Four data collections (4-Circle-Diffractometer at beamline D3, HASYLAB) have been carried out between the K- and L-absorption edges of Ta ($\lambda = 0.71 \text{ \AA}$, $\lambda = 0.56 \text{ \AA}$, $\lambda = 0.40 \text{ \AA}$, $\lambda = 0.237 \text{ \AA}$) on a sphere ($r = 0.065 \text{ mm}$) of cubic $KTaO_3$ ($a = 3.9885(2) \text{ \AA}$, Pm3m). The measurements at $\lambda = 0.237 \text{ \AA}$ were performed using an untuned Si-monochromator and suppressing the 111-reflection by 2 mm Aluminium. The four data sets comprised between 1243 ($\lambda = 0.71 \text{ \AA}$, $s_{max} = 1.315 \text{ \AA}^{-1}$) and 2071 ($\lambda = 0.40 \text{ \AA}$, $s_{max} = 1.978 \text{ \AA}^{-1}$) reflections yielding 163 to 474 unique reflections, all internal agreement indices $R_{int}(F^2)$ being between 0.019 and 0.029. The data processing included spherical absorption and TDS corrections.

Conventional refinements (6 parameters), both for all-data and high-order reflections ($s > 0.9 \text{ \AA}^{-1}$, without extinction), and a multipole refinement (14 parameters) for set III ($\lambda = 0.40 \text{ \AA}$) converged between $0.0087 \leq R \leq 0.0165$. The refined thermal dis-

placement parameters $u(K)$, $u(Ta)$, $u_{11}(O)$ and $u_{22}(O)$ were found systematically dependent on both wavelength and absorption coefficient. While the relative distribution of the u -values along the bonds remained unchanged, the individual values showed an approximately linear positive correlation with the absorption coefficient varying between $\mu = 426 \text{ cm}^{-1}$ and $\mu = 21.5 \text{ cm}^{-1}$. At present, there is no obvious explanation for this behaviour. Results of a detailed analysis being under progress will be presented.

PS02.01.15 MERIEDRIC TWINNING IN NEW $CoSi_3P_3$ SEMICONDUCTING COMPOUND. CRYSTAL STRUCTURE AND RAMAN SPECTROSCOPY. H. Vincent, J. Kreisel, O. Chaix-Pluchery and R. Madar LMGP (URA CNRS 1109), ENS de Physique de Grenoble, 38402 St Martin d'Hères, France.

New cobalt phospho-silicide $CoSi_3P_3$ has been synthesized and its crystal structure determined by single crystal X-ray diffraction. $CoSi_3P_3$ crystallizes with the apparent orthorhombic symmetry: $a = 5.900(1) \text{ \AA}$, $b = 5.703(1) \text{ \AA}$, $c = 12.736(1) \text{ \AA}$. Only one extinction rule is observed, it concerns reflections $0k0$ with $k = 2n+1$. Wilson statistic and non-linear optical tests excluding some symmetry center, attempt to solve the structure in $P2_212$ group was done but unsuccessful. Assuming the presence of pseudo 2_1 screw-axis along the other principal directions, crystal structure was then solved in the space group $P2_12_12_1$ by direct method and Fourier difference analysis.

Results of this first study being not very satisfactory, the crystal structure was refined in $P2_1$ space group, that is a subgroup of $P2_12_12_1$. This refinement did not give better results; crystallographic and weighted factors were so much mediocre $R = 0.065$, $R_w = 0.084$, and P and Si atom distribution on non-metallic sites was not clearly established. Polarized Raman spectra of single crystals confirming the monoclinic symmetry, meriedric twinning has been considered. A last refinement including four twinned domains gave much better results: agreement factors are $R = 0.037$, $R_w = 0.044$, and P and Si atoms are completely ordered on non-metallic sites.

The crystal structure can be described by zigzag chains of octahedra occupied by Co atoms and zigzag chains of tetrahedra occupied by P or Si atoms. All these infinite chains are parallel to the b-axis. Two chains of a same kind are separated each other by a chain of other kind. Magnetic susceptibility and electronic conductivity have been measured between 300 K and 10 K. $CoSi_3P_3$ is diamagnetic at room temperature and paramagnetic below 60 K. $CoSi_3P_3$ is semiconducting at room temperature with an energy gap of about 0.12 eV.

PS02.01.16 TRANS-5-HYDROXYCYCLOOCTYLTRIMETHYL STANNANE: A STRUCTURE IN SPACEGROUP Cc DESCRIBED AS A DISPLACIVE MODULATION OF A $P2_1/c$ PARENT STRUCTURE. A. C. Willis and A. D. Rae, Research School of Chemistry, Australian National University, Canberra, ACT, Australia, 0200

$(CH_3)_3SnC_8H_{14}OH$ crystallises in spacegroup Cc with 16 molecules per unit cell, a 13.786(4) b 13.856(3) c 28.917(2) \AA β 100.47(1) $^\circ$. An initial solution in spacegroup $P2_1/c$, $Z = 4$, used only the strong h even, k even reflections. This superimposes molecules separated by $a/2$ in the true structure. The Sn and 7 C atoms appeared as full weight atoms. The O and 4 remaining C atoms each appeared as a 1:1 disorder between sites separated by over 1 \AA . This was interpreted as two identical molecules related by a 120 $^\circ$ rotation about the $(CH_3)_3Sn - C$ bond. Ordering the disorder to create a model for the weak h odd, k odd reflections allows 4 possible structures. This is predicted from the doubly degenerate irreducible representation associated with the modulation vector a^*+b^* . Local inversion centres are maintained

and each structure may be described in terms of two c glide related sub-structures of $C-1$ symmetry. The coexistence of the substructures destroys the inversion as a symmetry element. Only half the c -glides of $P2_1/c$ are retained, the choice between halves selects between equivalent structures that are inversion related. Within the substructures only half of the inversion centres of $P2_1/c$ are retained and the choice between halves gives geometrically distinct options. Only the intensities of the weak extra reflections are sensitive to this choice, the wrong choice being unrefinable. The correct choice gave a sensible H-bonding network between O atoms while the other did not. Unconstrained refinement in spacegroup Cc creates difficulties for atoms that overlap in the average structure. This was overcome using features available in the Constrained Least Squares Refinement Program *RAELS92*. The 4 molecules in the asymmetric unit were constrained to have identical geometry that included a local mirror plane. This geometry was refined using local coordinates defined relative to refinable local orthonormal axial systems. Refinable *TLX* rigid body thermal parameterisation were used for each molecule, molecules inversion related in the substructure maintaining this relationship. The inversion symmetry of the substructures need not be maintained but departure from this was found to be minimal.

PS02.01.17 STRUCTURE DETERMINATION OF $PbZrO_3$ USING X-RAY ANOMALOUS DISPERSION. K. Yamasaki, Y. Soejima, Department of Physics, Kyushu University, Fukuoka 812-81, Japan, K. F. Fischer, Fachrichtung Kristallographie, der Universität des Saarlandes, D-66041 Saarbrücken, Germany (FRG)

On the basis of the method for superlattice structure analysis using X-ray anomalous dispersion, the intensity of several superlattice reflections from a $PbZrO_3$ single crystal have been re-examined: the intensity measurements were made as a function of incident X-ray energy around the Pb L_{III} and Zr K absorption edges. Since the structure factors of superlattice reflection are directly concerned with the displacement of anomalous scatterers from the higher symmetry position, they are expected to vary around the absorption edge when the anomalous scatterers have displacement. On the other hand, the structure factor is invariant when anomalous scatterers have no displacement. The experimental results show: Pb atoms have displacements only on the ab plane in the orthorhombic unit cell, and the pattern of the displacement is in anti-phase along the c direction. Zr atoms have an anti-phase type of displacements both on the ab plane and along c . These results support the structure determination by Glazer, Roleder and Dec (1993), except for the Zr displacement along c .

For refining our model, data were collected using 0.35 Å radiation up to $\sin\theta/\lambda=1.0 \text{ \AA}^{-1}$. To avoid a serious problem of domains, and to obtain information on the atomic displacement as precisely as possible, only superlattice reflections were used. The structure has been determined with R-factor 5 %: the results show anti-phase displacements of Zr atoms along c ; this is consistent with the results of the structure factor examination mentioned above. The present investigation requires that the antiphase type of displacement of Zr atoms must be considered.

PS02.01.18 INTERESTING INFORMATIONS FROM MODELING AND REFINEMENT OF DISORDERED MOLECULAR STRUCTURES. Hoong-Kun Fun and K.Sivakumar, X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia

Nowadays crystal structure determination of small molecules is nearly an automated process with little or no human intervention due to the availability of high speed computers and sophisticated software packages. However it is non-trivial when problems are faced in individual cases where the structure has some form of disorder. This then needs the role of a crystallographer for the careful analysis of the refinement results and to carry out the next step with reasoning. Analysis of the mode of disorder and suitably carrying out the refinement with constraints and restraints come with experience. In our laboratory, we have come across many such occasions with different types of disorder existing in the molecular structures. Some examples of disorders are those due to the conformational flexibility of certain rings and mixture of two isomorphous structures. A detailed survey of the disordered cases encountered in our laboratory and how the structures were refined will be discussed. The presentation will also include how to identify the minor conformational components present in the structure and model them to get better structural information.

PS02.01.19 SMALL CRYSTALS ARE OFTEN POOR CRYSTALS - WHY? Marjorie M Harding, Robert J Rule, Department of Chemistry, University of Liverpool PO Box 147, Liverpool L69 3BX, UK

Diffraction patterns recorded with synchrotron radiation have given us some clues. We have recorded synchrotron radiation diffraction data for structure determination for a substantial number of very small single crystals ($< 0.02 \text{ mm}$ for example). In most cases the use of synchrotron radiation was a 'last resort' because it had not proved possible to grow crystals of good size and quality suitable for use with conventional X-ray generators and diffractometers.

A large proportion of small crystals are either very thin plates or very fine needles; this is probably associated with poor growth in one or more directions in the structure. Three kinds of observation support this view:

a) For many of the small crystals studied because they would not grow bigger, the mosaic spread is unusually large (it can be quite accurately estimated in synchrotron radiation experiments because of the low beam divergence).

b) Following structure determination it is often possible to identify structural features which could explain the potential for faulted growth. Examples will be given.

c) The geometry of the Laue method for recording single crystal diffraction patterns is particularly sensitive to mosaic spread. By this method we have shown, for two compounds which form very fine needle crystals, that the mosaic spread is anisotropic, and is larger in the direction perpendicular to the needle axis than parallel to it. One structure is an aluminophosphate, with pores parallel to the needle axis; the other is organic, but also has large channels parallel to the needle axis.

So although synchrotron radiation has allowed structural information to be derived for a number of very small crystals, many of them were faulted. This prevented us from obtaining geometrical data of the highest quality, and probably also prevented them from growing larger.