PS02.01.13 TROUBLESOME PERCHLORATES.

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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 (Zachariasen, 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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PS02.01.14 A MULTIPLE WAVELENGTH STRUCTURE ANALYSIS OF KTaO3.

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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 (λ) = 0.71 Å, λ = 0.56 Å, λ = 0.40 Å, λ = 0.237 Å) on a sphere (r = 0.065 mm) of cubic KTaO3 (a = 3.9885(2) Å, Pm3m). The measurements at λ = 0.237 Å were performed using an untuned Si-monochromator and suppressing the 111-reflection by 2 mm Aluminium. The four data sets comprised between 1243 (λ = 0.71 Å, s_{max} = 1.315 Å^{-1}) and 2071 (λ = 0.40 Å, s_{max} = 1.978 Å^{-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 Å^{-1}, without extinction), and a multipole refinement (14 parameters) for set III (λ = 0.40 Å) converged between $0.0087 \leq R \leq 0.0165$. The refined thermal displacement 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 μ = 426 cm^{-1} and μ = 21.5 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 CoSi3P3 SEMICONDUCTING COMPOUND. CRYSTAL STRUCTURE AND RAMAN SPECTROSCOPY.

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New cobalt phospho-silicide CoSi3P3 has been synthesized and its crystal structure determined by single crystal X-ray diffraction. CoSi3P3 crystallizes with the apparent orthorhombic symmetry : a = 5.900(1) Å, b = 5.703(1) Å, c = 12.736(1) Å. 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 P22$_1$2 group was done but unsuccessfull. Assuming the presence of pseudo 2$_1$ screw-axis along the other principal directions, crystal structure was then solved in the space group P2$_1$2$_1$2$_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$_1$2$_1$2$_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. CoSi3P3 is diamagnetic at room temperature and paramagnetic below 60 K. CoSi3P3 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 P2₁/c PARENT STRUCTURE.

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(CH3)3SnC8H14OH crystallises in spacegroup Cc with 16 molecules per unit cell, a 13.786(4) b 13.856(3) c 28.917(2) Å β 100.47(1)°. 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 1Å. This was interpreted as two identical molecules related by a 120° rotation about the (CH3)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