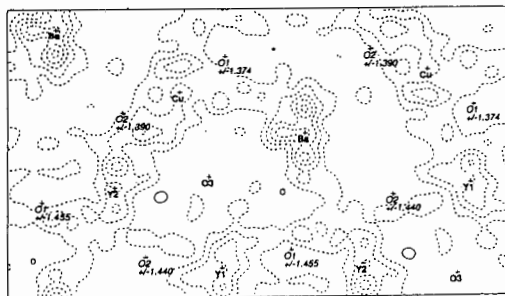


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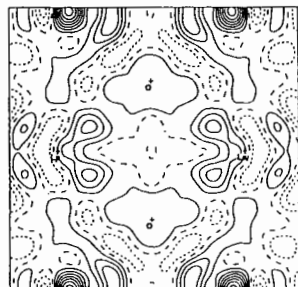


The effect is due to exchange depletion of valence electrons overlapping with closed electron sub-shells. The $\Delta\rho$ sections perpendicular to the $y/b = 0.25$ plane show relocation of density from within to above and below that plane. Atomic charges, determined by projecting $\Delta\rho$ onto atomic density basis functions (F L Hirshfeld, *Isr. J. Chem.*, 1977, 16, 198-201) are 2.8(1), 2.1(1), 1.6(1), 2.4(1), -1.8(1), -1.8(1), and -1.8(1) for Y1, Y2, Ba, Cu, O1, O2 and O3 respectively. The O atom charges are far more consistent than values determined earlier with Mo $K\alpha$ radiation. Those charges reflect partial transfer of valence electron density from cation to anion by exchange depletion.

The distances from each cation to the nearest neighbour O atoms are Y1 2.275(2)—2.379(1), Y2 2.302—2.355(1), Ba 2.611(2)—3.248(1) and Cu 1.974(1)—2.208(2) Å. Mean values are Y1—O 2.34(2), Y2—O 2.33(1), Ba—O 2.87(5) and Cu—O 2.04(6) Å. The topography of the deformation density can be understood only in terms of cation radii larger than those of the oxygen anions. Values of 1.79, 1.98, 1.34 and 1.16 Å for Y, Ba, Cu and O respectively used in the modelling the structure imply that the structural architecture for Y_2BaCuO_5 is determined by second-nearest-neighbour cation—cation interactions rather than anion—anion or cation—anion interactions. That model is supported by the vibration tensors, which are compact along the shorter cation-cation vectors, but extend along the anion-anion vectors. If exchange interactions are involved in the mechanism for high temperature superconductivity in the closely related $YBa_2Cu_3O_{7-\delta}$, it may be advisable to consider interactions beyond the first coordination sphere.

PS-14.02.14 DEFORMATION DENSITIES IN SIMPLE RARE EARTH COMPOUNDS By B. E. Eschtmann, E. N. Maslen, and N. R. Streltsova* *Crystallography Centre, University of Western Australia, Nedlands, 6009, Australia*

The deformation density $\Delta\rho$ for $LaOCl$ was determined for a naturally-faced single crystal measured with Mo $K\alpha$ radiation. The La coordination may be described as a mono-capped square antiprism. Neighbouring La atoms are connected by the oxygen double bridge shown (La-La 3.78Å).



There are $\Delta\rho$ peaks at the mid-point of a short La-Cl contact (3.76Å).

$\Delta\rho$ maps evaluated with extinction corrections that minimize differences between equivalent reflection intensities are closely approximated by those which optimize an extinction parameter as part of the least squares structure refinement.

Space group $P4/nmm$, tetragonal, $M_r = 190.36$, $a = 4.1218(8)$ Å, $c = 6.888(1)$ Å, $V = 117.03(6)$ Å³, $Z = 2$, $D_x = 5.402$ Mg m⁻³, $\mu_{Mo K\alpha} = 18.99$ mm⁻¹, $F(000) = 164$, $T = 293$ K, $R = 0.014$, $wR = 0.013$, $S = 1.87$ for 126 unique reflections.

Deformation densities for rare earth oxides and oxy-halides currently being studied with Mo $K\alpha$ ($\lambda = 0.71073$ Å) and with synchrotron radiation will be described.

PS-14.02.15 X-RAY STUDY OF THE ELECTRON DENSITY IN RHOMBOHEDRAL CARBONATES: $CaCO_3$, $MgCO_3$, $MnCO_3$. By E. N. Maslen, V. A. Streltsov* and N. R. Streltsova, *Crystallography Centre, University of Western Australia, Australia.*

Calcite, $CaCO_3$, is an abundant carbonate mineral. Its structure is isomorphous with that of several carbonate mineral constituents of sedimentary rocks, including magnesium- and transition metal-bearing carbonates. The calcite structure has the same space group, $R\bar{3}c$, as another widely distributed mineral, corundum ($\alpha-Al_2O_3$), a benchmark compound for which the electron density has been measured several times over the past decade. A sketch of the calcite structure coordination close to the cations is shown in Fig.1. The deformation electron density ($\Delta\rho$) in naturally-faced single crystals of synthetic $CaCO_3$ and the minerals: magnesite, $MgCO_3$, and rhodochrosite, $MnCO_3$, was determined using diffraction data measured with Mo $K\alpha$ ($\lambda = 0.71073$ Å) and 0.7Å synchrotron X-radiation. A specimen of $CaCO_3$ grown directly from aqueous solution was bounded by two $\{104\}$, two $\{1\bar{1}4\}$, two $\{0\bar{1}4\}$ and one $\{1\bar{2}3\}$ faces with dimensions $31 \times 36 \times 46 \times 37 \mu m$ respectively from the crystal centre. Cleavage fragments of $MgCO_3$ and $MnCO_3$ mineral rocks were bounded by the same first six faces with dimensions $24 \times 55 \times 77 \mu m$ and $40 \times 24 \times 49 \mu m$ respectively from the crystal centres. Sets of structure factors for synchrotron radiation and Mo $K\alpha$ tube radiation for these crystals are consistent. Extinction corrections that minimize differences between equivalent reflection intensities (Maslen and Spadaccini, *Acta Cryst.*, 1993, in press) have been applied. This correction ($y_{min}=0.80$) for $CaCO_3$ is closely approximated by the values which optimize the extinction parameter as part of the least squares structure refinement. The extinction effect for $MgCO_3$ was small ($y_{min}=0.96$). No extinction was observed for $MnCO_3$. A map of $\Delta\rho$ through the CO_3 group in the (0001) plane for $CaCO_3$ from X-ray tube data is shown in Fig.2. The general topographies of the $\Delta\rho$ maps are broadly similar for all the carbonates studied. There are $0.26e\text{\AA}^{-3}$ high density maxima in the C-O bonds and $0.28e\text{\AA}^{-3}$ maxima at the O-atom lone pairs. Corresponding values of $\Delta\rho$ for $MgCO_3$ and $MnCO_3$ are $0.58e\text{\AA}^{-3}$ and $0.80e\text{\AA}^{-3}$ in the C-O bonds, and $0.40e\text{\AA}^{-3}$ and $0.50e\text{\AA}^{-3}$ at the O-atom lone pairs. The maxima in the $\Delta\rho$ maps for $CaCO_3$ are lower than those for $MgCO_3$ and $MnCO_3$. This can be attributed to greater exchange depletion when the more diffuse radial electron distribution of the Ca cation overlaps with the CO_3 group. Aspherical charge distribution around the d-metal Mn can be related to the octahedral crystal field. Atomic charges determined by projecting $\Delta\rho$ onto atomic density basis functions (Hirshfeld, 1977, *Isr. J. Chem.*, 16, 198-201) are Ca +0.16(2)e, C +0.23(2)e and O -0.13(1)e for $CaCO_3$, and Mg +0.06(2)e, C +0.21(2)e and O -0.09(1)e for $MgCO_3$ and Mn +0.43(5)e, C +0.17(4)e and O -0.20(1)e for $MnCO_3$.

X-ray tube data at $T=293$ K, Space group $R\bar{3}c$, hexagonal, $Z=6$: $CaCO_3$, $M_r=100.09$, $a=4.991(2)$ Å, $c=17.062(2)$ Å, $V=368.1(3)$ Å³, $D_x=2.709$ Mg/m³, $\mu_{Mo K\alpha}=2.134$ mm⁻¹, $F(000)=300$, $R=0.017$, $wR=0.023$, $S=4.52$, 328 unique reflections; $MgCO_3$, $M_r=84.31$, $a=4.635(1)$ Å, $c=15.023(2)$ Å, $V=279.5(1)$ Å³, $D_x=3.005$ Mg/m³, $\mu_{Mo K\alpha}=0.59$ mm⁻¹, $F(000)=252$, $R=0.022$, $wR=0.027$, $S=6.59$, 332 unique reflections; $MnCO_3$, $M_r=114.95$, $a=4.773(1)$ Å, $c=5.642(1)$ Å, $V=308.6(1)$ Å³, $D_x=3.71$ Mg/m³, $\mu_{Mo K\alpha}=5.85$ mm⁻¹, $F(000)=330$, $R=0.019$, $wR=0.028$, $S=3.23$, 368 unique reflections.

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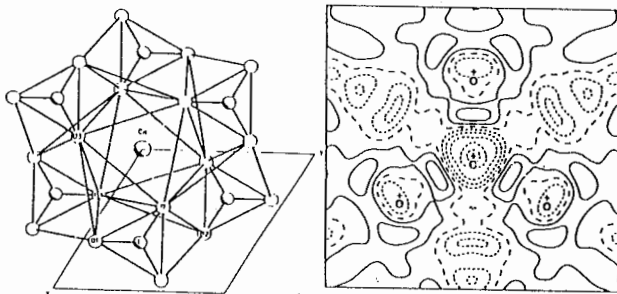
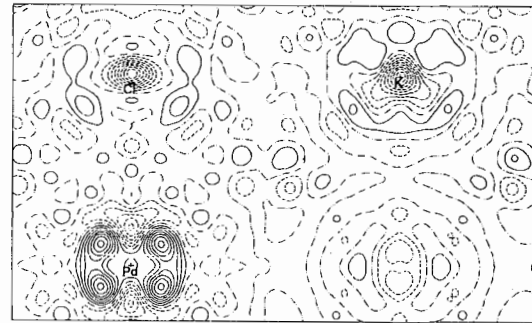
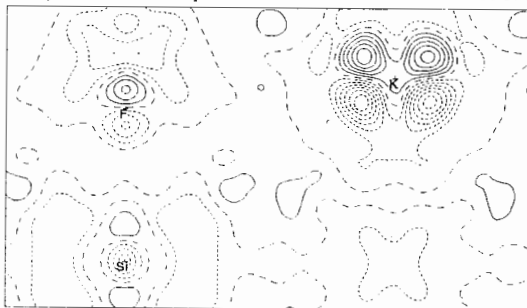


Fig. 1

Fig. 2

Figure 2: $\Delta\rho$ in [110] plane of K_2PdCl_6 . Borders $6.6\text{\AA} \times 4.0\text{\AA}$, contours $0.2e\text{\AA}^{-3}$.

PS-14.02.16 ACCURATE ELECTRON DENSITY IMAGING OF K_2MH_6 COMPOUNDS. By J. R. Hester, Crystallography Centre, University of Western Australia, Nedlands 6009, Australia. Accurate electron densities of K_2SiF_6 and K_2PdCl_6 have been obtained using synchrotron radiation, providing detailed information on the atom-atom interactions in these structures. X-ray data was collected from crystals on conventional sources and at the Photon Factory synchrotron. Although the electron densities for the two compounds are topographically similar, they contain unexpected features. In the K_2SiF_6 maps (Fig. 1) the density is depleted within the SiF_6 moiety. The density near the K is strongly depleted along the K-Si vectors. The density is also depleted along the non-bonded K-K and F-F vectors. Electrons accumulate in regions close to the K atom and in a broad interatomic "sea", delineated by the zero contour in Fig. 1. The $\Delta\rho$ topography near K is similar in the room temperature K_2PdCl_6 map. If the anomalous features around K in each case are due to anharmonic thermal vibrations, these should diminish at low temperatures. A low temperature K_2SiF_6 data collection, while quite noisy, shows evidence of the persistence of this feature, as also does the relevant section (Fig. 2) based on low temperature K_2PdCl_6 data of Takazawa, H., Ohba, S. & Saito, Y. [(1988) *Acta Cryst.*, B44, 580-585]. The K electron density indicates that exchange effects between second-nearest neighbours are important in this structure. Overlap of the atoms in the SiF_6 moiety forces electrons out of the volume surrounding the nuclei into interatomic regions. The effects of K-K and Cl-Cl overlap are predictably weaker in the less tightly packed K_2PdCl_6 structure. A calculation of atomic charges based on projection of $\Delta\rho$ onto atomic density basis functions partitions the two difference densities quite differently, so that the signs of the K_2PdCl_6 charges agree with their formal values whereas the signs of the K_2SiF_6 charges are reversed. This is mainly due to the changes in atomic radii partitioning the interatomic sea differently. It is clear that the same physical processes are responsible for both electron distributions.

Figure 1: $\Delta\rho$ in [110] plane of K_2SiF_6 . Borders $5.6\text{\AA} \times 3.3\text{\AA}$, contours $0.1e\text{\AA}^{-3}$. Negative - dotted, positive - solid, zero - dashed.

14.03 - X-ray Physics, Diffraction and Absorption

PS-14.03.01 X-RAY POLARIZATION PHENOMENA IN PERFECT AND IMPERFECT CRYSTALS.

By H.R.Höche, C.Eisenschmidt, H. Höfer and W.Leitenberger, Fachbereich Physik, Martin-Luther-University Halle, Germany

It can be seen in highly resolved X-ray diffraction experiments that the polarization state of linearly polarized X-radiation is changed.

The polarization state is not changed by BRAGG-case diffraction in perfect crystals if the polarization plane is parallel or perpendicular to the diffraction plane. In all other relations between diffraction plane and polarization plane the polarization of the diffracted beam is dependent on the angular position in the interference range (rocking curve). A systematical polarization mixing was found in experiments with a Si crystal containing a high density of dislocations which were produced by a high temperature deformation.

The polarization state is unchanged also by LAUE-case diffraction in perfect crystals if the polarization plane of the incident beam is parallel or perpendicular to the diffraction plane. In all other relations of these two planes four X-ray waves are excited inside the perfect crystal. In general the diffracted beam is elliptically polarized, it is caused by the different absorption coefficients (BORRMANN-effect). The polarization state depends on the crystal thickness and on the angular position in the interference range (BORRMANN-fan). The experiments were done with synchrotron radiation at HASYLAB (DESY Hamburg). The experimental results are in good agreement with the dynamical theory of X-ray diffraction. There are a phase difference between the σ - and π -polarized waves in the transmitted beam also. Especially in the centre of the BORRMANN-fan this phase difference can be used for the construction of a polarization optical phase shifter. Theoretical and first experimental results will be presented in detail.

This work was supported by the BMFT under the project Nr. 05 SNHAAB 0.

PS-14.03.02 HIGH RESOLUTION POWDER DIFFRACTOMETRY WITH A BENT PERFECT CRYSTAL MONOCHROMATORS.

By P. Mikula*, M. Vrána, P. Lukáš, Nucl. Phys. Inst., 250 68 Řež, Czech Republic, V. Wagner, PTB, 3300 Braunschweig, Germany and B. Alefeld, KFA, 5170 Jülich, Germany.

We are presenting a highly efficient diffraction arrangement with a cylindrically bent perfect crystal monochromator suitable particular-