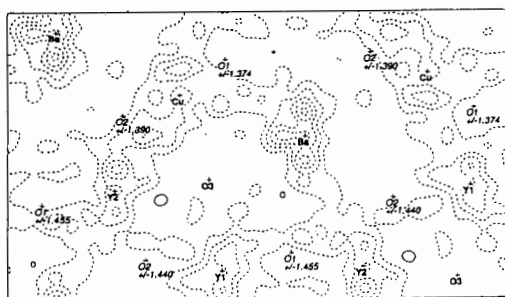


14-Diffraction Physics and Optics

382

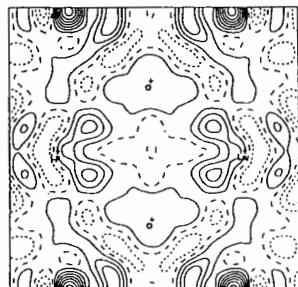


The effect is due to exchange depletion of valence electrons overlapping with closed electron sub-shells. The $\Delta\rho$ sections perpendicular to the $y/b = 0.25$ plane show relocation of density from within to above and below that plane. Atomic charges, determined by projecting $\Delta\rho$ onto 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, $D_x=3.711$ 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.