

06.4-1 ELECTRON DENSITY IN THE ALKALI-HALIDE CRYSTALS IN LDA (Local Density Approximation). By G. Böbel, P. Cortona and F.G. Fumi, Dipartimento di Fisica, Università di Genova e CISM/MPI-GNSM/CNR, Unità di Genova, Italy.

We have calculated (G. Böbel, P. Cortona, C. Sommers and F.G. Fumi, Acta Cryst., 1983, A39, 400; Acta Cryst., 1985, A41, 175; Acta Cryst., 1985, A41, 618) the electron density in the four 'isoelectronic' alkali-halide crystals (NaF, KCl, RbBr, CsI) by the method of augmented-spherical waves (ASW) in the self-consistent local-density-approximation to the density-functional theory (LDA). We have verified the good quality of the computed electron density by evaluating the heats of formation of the salts from total energy calculation, then computed structure factors for the lower-order 'sum' and 'difference' reflections, the latter being particularly sensitive in ionic deformations. The computed LDA structure factors for the 'sum' reflections agree well with those obtained from Hartree-Fock (HF) free-ion wavefunctions, while those for the 'difference' reflections are smaller than the HF values. This points to a 'contraction' of the anion and a 'dilation' of the cation in passing from free ions to ions in crystals. The contraction of the anion in NaCl has, in fact, been found also from pseudopotential LDA calculations (W. Andreoni, K. Maschke and M. Schlüter, 1982, Phys. Rev., B26, 2314) and from Lowdin-type HF calculations (F. Gygi, K. Maschke, and W. Andreoni, 1984, Solid State Comm., 49, 437).

For KCl, the fitting of the computed LDA structure factors for the 'sum' reflections to the recent  $\gamma$ -ray data by M.C. Schmidt, R. Colella and D.R. Yoder-Short (1985, Acta Cryst., A41, 171) with a single Debye-Waller factor, gives also excellent agreement with the only 'difference' reflection measured by Schmidt et al. (the 111 reflection).

For NaF, the same holds true for several difference reflections from the X-ray data by Howard and Jones (1977, Acta Cryst., A33, 776) while an unexplained discrepancy remains with the (early)  $\gamma$ -ray data by Yoder and Colella (1982, Phys. Rev., B25, 2545).

For RbBr and CsI we have been unable to find accurate experimental data. In 1977, Zunger and Freeman (Phys. Rev., B16, 2901) had already reported structure factors computed in LDA with the self-consistent (non-muffin-tin) LCAO method for LiF and their results have recently been found to be in good agreement with the  $\gamma$ -ray data by Schmidt et al. (see Böbel et al., 1985, Acta Cryst., A41, 175).

More recently, Jansen and Freeman (1986, Phys. Rev., B33, 8629) have reported structure factors for NaCl computed in LDA with the full-potential linearized augmented-plane-waves method (FLAPW), which includes non-spherical components of the lattice potential which are ignored in our ASW calculations. They find large discrepancies (up to 100%) with (relatively old) experimental X-ray structure factors for the high-order 'difference' reflections, using the theoretical Debye-Waller factors for Cl<sup>-</sup> and Na<sup>+</sup> given by Schocknecht (1957, Z. Naturforsch., 12, 983). We note however that the experimental Debye-Waller factors by Witte and Wölfel (1955, Z. Phys. Chem., 3, 296) or by Renninger (1952, Acta Cryst., 5, 711) eliminate the disagreement for the high-order 'difference' reflections without affecting the agreement for the 'sum' reflections.

Finally we should like to emphasize that Froyen and Cohen (1984, Phys. Rev. B, 29, 3770) have been able to account from first principles for the high pressure phase transition of NaCl to the CsCl structure by using the electron density computed by pseudopotential LDA methods which include non-spherical components of the potential for the valence electrons (i-dependent pseudopotentials).

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06.4-2 EXPERIMENTAL AND THEORETICAL STUDY OF MAGNETICAL PROPERTIES OF CHAIN SILICATES. By S. Nagel, S.S. Hafner and H. Maghsudnia, Institute of Mineralogy, University of Marburg, D-3550 Marburg, W-Germany.

In chain silicates of the pyroxene type with compositions (Ca,Fe,Mg)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, Ca, Fe, and Mg are located in edge-sharing M1 and M2 polyhedra which form ribbons of infinite length parallel to the c axis. In general, the M1 polyhedra (general positions) are fairly regular octahedra whereas the M2 polyhedra (general positions) are more distorted octahedra when Ca-free and 7-8 fold coordinated when enriched in Ca. Neutron diffraction studies revealed strong ferromagnetic ordering of Fe<sup>2+</sup> within the ribbons and weak antiferromagnetic ordering between the ribbons. Previously reported data and additional measurements not yet published allow the following comprehensive summary:

The Neel temperatures T<sub>N</sub> are 45 K for orthorhombic Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> and 41 K for monoclinic CaFeSi<sub>2</sub>O<sub>6</sub>. In CaFe<sub>1-x</sub>Mg<sub>x</sub>Si<sub>2</sub>O<sub>6</sub> solid solutions, T<sub>N</sub> drops to 34 K for x=0.2 and 26 K for x=0.3. Moreover, T<sub>N</sub> is reduced considerably if part of Fe<sup>2+</sup> is substituted by Mn<sup>2+</sup>. The magnetic moments for Fe are known to be different at the different positions. They are 4.1  $\mu_B$  at M1 and 3.3  $\mu_B$  at M2, respectively, in Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, and  $\approx$ 3.4  $\mu_B$  at M1 in CaFeSi<sub>2</sub>O<sub>6</sub>. The isomer shifts and nuclear quadrupole splittings of <sup>57</sup>Fe determined from Mössbauer spectra are systematically smaller at M2 than at M1. Further, the hyperfine fields H<sub>eff</sub> are significantly different at M1 and M2 and for different compositions. They are 70 kOe at M1 and 319 kOe at M2 in orthorhombic Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, 210 kOe at M1 in CaFeSi<sub>2</sub>O<sub>6</sub> and 220 kOe in CaFe<sub>1-x</sub>Mg<sub>x</sub>Si<sub>2</sub>O<sub>6</sub> (x=0.2). The dependence of H<sub>eff</sub> on x is also known. The signs of the quadrupole splittings at M1 and M2 are known from <sup>57</sup>Fe spectra at 4.2 K and from spectra in applied magnetic fields at temperatures above T<sub>N</sub>. Detailed information about the dependence of the quadrupole splittings on temperature is available for several compositions.

These results may be understood from the different local distortions of the M1 and M2 polyhedra in chain silicates if one assumes considerable importance of covalency between Fe 3d and O2p orbitals. In order to provide a quantitative understanding, cluster calculations have been performed using the Multiple Scattering X<sub>c</sub> technique. The cluster wave functions which emerge from these calculations have been used to obtain theoretical values for local magnetic moments, hyperfine parameters of <sup>57</sup>Fe, as well as crystal field splittings. A similar theoretical approach has been previously applied to Fe<sub>2</sub>O<sub>3</sub> where it was possible to obtain excellent agreement with the experimental results for isomer shift, quadrupole splitting and magnetic hyperfine field. Although in the present case the size of the calculated clusters had to be quite limited because of absent symmetry at the general M1 and M2 positions, the results are found to be most helpful for the interpretation of the experimental data.