

06.2-13 BONDING AND LONE-PAIR DENSITY IN TETRAFLUOROTEREPHTHALONITRILE, $C_6F_4(CN)_2$. By J. D. Dunitz, W. B. Schweizer and P. Seiler, Laboratorium für Organische Chemie, ETH-Zentrum, CH-8092 Zürich, Switzerland.

The crystal structure of tetrafluoroterephthalonitrile $C_6F_4(CN)_2$ has been determined at room temperature by van Rij and Britton (Cryst. Struct. Comm. 10, 1981) who pointed out that this compound (space group $Cmca$, $Z = 4$, molecular symmetry $2/m$) is an excellent candidate for a careful bonding-density study at low temperature.

We have measured two data sets at 98 K; a "normal" set extending to $\sin\theta/\lambda = 0.8 \text{ \AA}^{-1}$, b) a more accurate (8 equivalent reflexions) and more extensive set extending to $\sin\theta/\lambda = 1.15 \text{ \AA}^{-1}$. For set (a) we used exponentially modified weights (Dunitz and Seiler, Acta Cryst. A29, 589, 1973) with $r = 5 \text{ \AA}^2$; for set (b) we tried several weighting systems and finally chose $\omega = (\omega_{\text{obs}} e^{as^2}) / (b + e^{as^2})$ with $b = 2 \times 10^4$, $a = 36 \text{ \AA}^2$, an expression which gives effectively constant weight to reflections with $s > 0.6 \text{ \AA}^{-1}$ but without the discontinuity introduced in conventional high-order refinement based on a step-function. Bond distances derived from the two independent data sets agree within 0.003 Å, U^j values within 0.0013 Å². Difference X-X maps show clearly defined bonding density for all bonds except the highly polar C-F bond, which is almost featureless for both data sets. The map for set (b) shows a well defined lone-pair density at N as well as extremely diffuse density around the F atom.

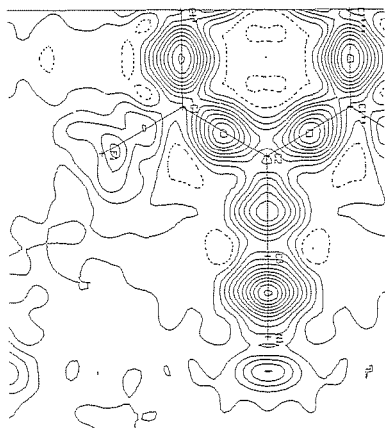


Figure X-X density in molecular plane. Contours at intervals of $0.075 e. \text{ \AA}^{-3}$.

The contrast between the well defined bonding density in homopolar C-C bonds and the relative absence of bonding density in the C-F bond is striking.

06.2-14 ANALYSIS OF NET ATOMIC CHARGES IN TRANSITION METAL CARBONYLS BY A POLYHEDRAL SPACE PARTITIONING TECHNIQUE.* By A. Holladay, P. Leung, G. Moss & P. Coppens, Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214

A space partitioning algorithm based on space-filling polyhedral volumes surrounding each atom (P. Coppens & T. N. Guru Row, Ann. N.Y. Acad. of Science (1978) 313, 244) has been applied to a number of transition-metal carbonyl complexes. The average electron density per unit volume at the surface of the polyhedron is given by dQ/dV , where dQ is the change in the integrated total electron density upon increasing polyhedron size and dV is the associated increase in volume. dQ/dV shows a minimum as a function of the position of the polyhedron boundary which is located about halfway between the transition metal and the adjacent carbon atom. The corresponding definition of atomic volume leads to a negative charge of about 0.4 electrons on each of the cobalt atoms in $Co_3(CO)_9CH$ when integration is performed on the deformation density, but a charge of about +1 electrons when the total observed density is integrated. The difference is even more pronounced for $Cr(CO)_6$ for which charges of -0.4 and +4.0 are obtained for integration on $\Delta\rho$ and ρ_{obs} respectively. The discrepancy can be understood by examination of integration results on isolated Co and Cr atoms which show most of the 4s and part of the 3d electron density to be outside the defined volume of integration.

Since the bonded atom is more negative than the spherical atom in the promolecule the conclusion is reached that the transition metal atoms investigated are slightly negative. The results are in general agreement with net charges obtained with the kappa refinement least squares technique which uses a quite different definition of the atomic volume.

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06.2-15 AN ELECTRON-DENSITY STUDY OF TiC. By A. Dunand, H.D. Flack and K. Yvon, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland.

Titanium monocarbide is a hard, brittle, refractory metallic solid ($T_m \sim 3200^\circ\text{C}$) which has the NaCl type structure. In order to study its bonding, deformation density maps were calculated from experimentally measured X-ray intensities of a nearly spherical single crystal ($\bar{r} = 84(2) \mu\text{m}$) of composition $TiC_{0.940(5)}$ * ($a = 4.3295(1) \text{ \AA}$, 1464 reflexions with $\sin\theta/\lambda \leq 1.31 \text{ \AA}^{-1}$, Nb filtered MoK_α radiation, ω - 2θ step scans, 0.01°s^{-1}).

After averaging symmetry equivalent reflexions (internal consistency $R = 0.012$) a set of 59 unique reflexions was obtained. A least-squares refinement of the scale factor (k), two temperature factors ($U(Ti)$, $U(C)$), one occupancy factor ($p(C)$) and an isotropic type extinction parameter (g) using scattering factors of neutral atoms and including all observed reflexions gave an agreement index $R_w = 0.007$ ($GoF = 6.7$).

The parameters obtained are $U(Ti) = 0.00324(4) \text{ \AA}^2$, $U(C) = 0.0030(2)$, $p(C) = 0.91(1)$, $g = 39(1)$, $\sigma(k)/k = 0.005$. The correlation coefficients greater than 0.5 are $c(k, g) = 0.90$, $c(k, U(Ti)) = 0.95$, $c(g, U(Ti)) = 0.81$ and $c(p(C), U(C)) = 0.92$.

A high-order refinement ($0.60 \leq \sin\theta/\lambda \leq 1.31$) did not produce significantly different results.

The deformation density map shown in Fig. 1 was calculated from high order data only ($\sin\theta/\lambda > 0.6 \text{ \AA}^{-1}$). Clearly, the 3d contribution to the scattering persists at large Bragg angles, revealing sharp bonding features of e_g symmetry around the Ti atom sites. These are con-

sistent with the postulated strong metal - non metal interactions in this compound.

In contrast, no significant distortions from spherical symmetry are observed around the C atom sites.

A AgK_{α} data set is currently being measured to confirm these features.

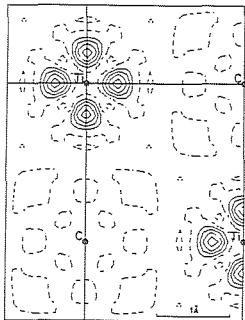


Fig. 1 : Deformation density of TiC in the (100) plane. Ti and C atoms sites, symmetry is $m\bar{3}m$. Contour intervals at $0.1 e/\text{\AA}^3$. Zero and negative contours broken.

* The crystal was kindly provided by Dr. Politis, at the Kernforschungszentrum Karlsruhe.

06.2-16 EXPERIMENTAL STRUCTURE FACTORS OF ZnSe. By R. Uno, Y. Ohgiri, M. Nakajima and J. Ishigaki, College of Humanities and Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156, Japan.

The experimental structure factors of ZnSe were obtained from an X-ray measurement performed by P.M. Raccach et al (Phys. Rev. 148(1966) 904). Among the factors, those of the difference lines, where $h+k+l=4n+2$, are appreciably larger than those theoretically calculated by using self-consistent OPW model (Phys. Rev. B1(1970) 756).

Since the difference lines overlap with the tail of stronger lines, separation of the difference lines from the adjacent stronger lines was made, in the present work, according to the profile-fitting method, by the use of parameters determined from well-separated lines. Preliminary results shows that the structure factors of the difference lines at low Bragg angles, such as F(200) and F(222), are not larger than the theoretical values. This will give considerable influence to the solid state effect on the electron distribution of atoms in ZnSe.

06.2-17 THE X-RAY STUDY OF ELECTRON DENSITY DISTRIBUTION IN REAL SPACE IN IONIC-COVALENT STRUCTURES $A''B''$ AND ITS INFLUENCE ON SPECTRUM CHARACTERISTICS. By J. Jakimavichus, R. Purlys and A. Shirvaitis, Faculty of Physics, Vilnius University, Vilnius, Lithuania USSR.

Electron density distribution of valence electrons in real space and its influence on effective ion charges, lattice potential and energy level components of zone structure electron spectra have been investigated in cubic (ZnS, ZnSe, CdTe) and hexagonal (CdS, CdSe, ZnO) structures. Lattice electron density and ion distributions have been obtained by Fourier transform of structure amplitudes and form factors, measured by X-ray from CuK_{α} . For the construction of potential components and calculation of energy levels the technique of (J. Jakimavichus, J. Batarūnas, Phys. Molecules, (1976) Nr. 2, 61) has been used. Valence electron density increase in the regions of principal maximums of valence electrons wave function have been shown in crystals. The electron density change in crystals was found to be bigger compared with its theoretical investigation taking into account atom ionization and excitation to valence state. This change causes the increase of effective ion charges and the decrease of structure amplitudes and potential components (200) and (011) in cubic and hexagonal structures respectively. This, in its turn, conditions the decrease of conductivity zone lower levels and diminution of the forbidden zone width. The reduction of conductivity zone levels has been shown to become smaller with the increase of bond ionicity of the investigated compounds $A''B''$.

06.2-18 NEUTRON AND X-RAY DIFFRACTION STUDY OF THE CRYSTAL STRUCTURE OF SiP_2 . By T. Chattopadhyay, and H.G.v. Schnering, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 7000 Stuttgart 80, Federal Republic of Germany

Neutron diffraction data have been collected from SiP_2 single crystal with pyrite structure at 60, 120 and 293 K. The positional and thermal parameters have been obtained at these temperatures by refining them with these intensity data. The conventional agreement factors for these refinements are $R=0.044$, 0.060 and 0.076 at 60, 120 and 293 K respectively. The variation of the structural parameters with temperature have been studied and discussed. Accurate X-ray diffraction data have been collected from a spherical SiP_2 single crystal at 293 K up to $\sin\theta/\lambda=1.2 \text{\AA}^{-1}$. Calculations of valence and deformation densities } X-N are in progress and will be presented at the meeting. The isotropic temperature parameters of Si and P atoms obtained from neutron diffraction studies vary linearly with temperature. The mean square vibrational amplitudes of Si and P atoms are practically the same at low temperature, but at the room temperature the mean square amplitude of Si atom is found to be larger than that of P atom.