

06.X-1 PAST AND PROJECTED USE OF ACCURATE STRUCTURE FACTORS By P. Coppens, Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14214 USA.†

Applications of the use of accurate structure factors to charge density mapping, multitemperature studies of thermal motion, the study of phase transitions and ion transport in solids will be reviewed. As structure factors used may be accurate to about 1%, while weaker reflections are much less accurate most quantitative applications are experimental error-limited. Even for silicon for which much more accurate Pendellösung reflections are available conclusions are affected by uncertainties in the weak reflection intensities. Since highly intense, highly collimated short wavelength X-ray sources are becoming available, we may anticipate a reduction in absorption, extinction, data truncation and crystal quality effects. What new applications will be realized if structure factor accuracy can be improved by say a factor five and "weak" reflections can be measured to an accuracy of say 1%? In the field of electron densities we may study the effects of intermolecular interactions, now on the borderline of observability, observe deviations from transferability of group densities and more generally provide a critical analytical tool for assessment of ground state properties of molecules and crystals. The enhancement of accuracy combined with increase of resolution to  $3\text{-}4\text{\AA}^{-1}$  and the ability to analyze weak spherical atom-forbidden reflections in crystals of high symmetry will allow much more stringent analysis of thermal motion formalisms and anharmonic contributions. Other potential applications will be discussed.

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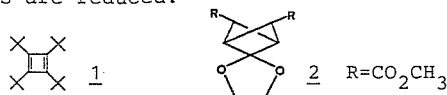
06.X-2 DETERMINATION OF ACCURATE INTENSITIES AND STRUCTURE FACTORS : APPLICATION WITHIN THE INORGANIC CHEMISTRY FIELD. By D. Schwarzenbach, Institut de Cristallographie, Université de Lausanne, CH - 1015 Lausanne, Switzerland.

A routine structure determination consists in the localization of the maxima of the electron density. Accurate structure factors thus serve to yield more detailed spatial pictures of this function which are the topic of another micro-symposium. Most inorganic framework structures contain more (Ca to U) or less (Mg to Cl) heavy elements. In addition, many of them are so simple that some of their reflections have very high intensities. The relationship between these intensities and the accurate structure amplitudes tends to be obscure, the latter not being measurable quantities. On the other hand, data with very high resolution can easily be measured for these structures, up to  $(\sin\theta/\lambda)_{\text{max}} = 1.75\text{\AA}^{-1}$ , TDS then being important even for the hardest compounds. Our charge density and cumulant refinements of rutile ( $\text{TiO}_2$ ) and cuprite ( $\text{Cu}_2\text{O}$ ) result in excellent agreements with the measured data ( $R = 0.007$ ), but apart from the difficulties of the physical interpretation of the results, a puzzling problem remains : the g.o.f.  $\frac{1}{N} \sum w(\Delta F)^2$  as a function of  $\sin\theta/\lambda$  increases moderately for  $\text{TiO}_2$  and strongly for  $\text{Cu}_2\text{O}$  above  $1.6\text{\AA}^{-1}$ . Individual  $\Delta F$ 's are both negative and positive. Are we starting to observe deformations of the atomic core ? Would neutron data of comparable accuracy and resolution show no such effect ?

06.X-3 BENT BONDS IN FOUR-MEMBERED RINGS

By H. Irngartinger, M. Nixdorf and W. Reimann, Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Bundesrepublik Deutschland.

The X-X deformation densities of the four-membered ring systems of tetra-tert.-butyl-cyclobutadiene **1** (H. Irngartinger and M. Nixdorf, *Angew. Chem.* **95**, 415 (1983)) and of a bicyclo-[1.1.1]pentane derivative **2** have been determined. The X-ray data were collected at low temperature (1:123; 2:99 K). Up to  $\sin\theta/\lambda = 1.15\text{\AA}^{-1}$  symmetrically equivalent reflections were measured and averaged. All the bonds of the four-membered rings are bent. The electron density maximum of the single bond in **1** is shifted by  $0.2\text{\AA}$  from the bond axis. The corresponding value of the stronger C=C double bond is only half as large. The highly strained bridged system of **2** shows deviations of  $0.15\text{\AA}$  of the bonding density maxima from the bond axes. Despite the very short 1...3-distance of  $1.923\text{\AA}$  in **2** no electron density is appearing along this nonbonding contact. Therefore indications for back lobe interactions could not be detected. In contrast to the room temperature structure of **1** (H. Irngartinger, et al., *Angew. Chem.* **92**, 214 (1980)) the non-square form of the four-membered ring is definitely proven by the low temperature data, because disorder effects are reduced.



06.X-4 THEORETICAL INTERPRETATION OF CHARGE DENSITIES. By Michael B. Hall, Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

As experimental determinations of the charge densities become more and more accurate, the need for theoretical calculations will increase. Not only is it pleasing and convincing to see a similarity between the experimental and theoretical results, but the theoretical charge density can be manipulated in ways that are nearly impossible for the experimental density. This advantage is crucial since in forming either the experimental or the theoretical deformation density one arbitrarily subtracts spherical atoms. However, in interpreting the electron density distribution it might be useful to subtract atoms in prepared valence states or to subtract molecular fragments. The latter is particularly helpful if one wishes to concentrate attention on the formation of a particular bond. We will present a number of examples of the difference between subtracting spherical atoms, non-spherical atoms, or molecular fragments. We will also present some recent theoretical results on metal-to-metal and metal-to-carbon bonds.