

06.2-22 CRYSTAL STRUCTURE AND ELECTRON DENSITY STUDIES OF THE TWO MODIFICATIONS OF TETRACYANOETHYLENE (TCNE). By U. Drück, H. Guth, E. Hellner, Institut für Mineralogie, H. Dannöhl and A. Schweig, Fachbereich Physikalische Chemie, Sonderforschungsbereich 127 "Kristallstruktur und Chemische Bindung", Universität Marburg, D-3550 Marburg, FRG and G. Heger, Kernforschungszentrum Karlsruhe, Institut für Angewandte Kernphysik I, D-7500 Karlsruhe, FRG.

Electron density studies of the two modifications of TCNE are part of a project on experimental and theoretical investigations of electron density distributions in crystals of organic compounds. Within this project we studied TCNE at 120K in both modifications reported in literature (Drück, U. & Guth, H., Z. Krist. 161, 103, 1982 and Becker, P., Coppens, P. & Ross, F.K., JACS, 25, 7604, 1973). Crystal data (120K):  $P2_1/n$ ,  $Z=2$ ,  $a=7.366(3)$ ,  $b=6.133(2)$ ,  $c=6.935(3)$  Å,  $B=97.17(2)^\circ$  and  $Im\bar{3}$ ,  $Z=6$ ,  $a=9.628(3)$  Å.

X-ray and neutron data sets were collected on automated four cycle diffractometers at room temperature and 120K (for cubic TCNE only X-ray data so far). The final agreement factors are 0.035 and 0.033 (TCNE monoclinic, RT), 0.037 and 0.034 (TCNE monoclinic, 120K), 0.034 and 0.024 (TCNE cubic, RT); the 120K results are still in progress. Two different models, one based on a charge cloud model, one on a multipole expansion, were applied to the data. These results will be shown together with X-X and X-N syntheses. They will be compared with the electron density maps of p-dicyanobenzene and hexacyanobenzene.

4-31G+BF AHF dynamic deformation densities will be presented for TCNE and p-dicyanobenzene (for the methods, see: A. Schweig and coworkers in "Electron Distributions and the Chemical Bond", P. Coppens and M.B. Hall, eds., Plenum Press, 1982, p. 255 and Int. Rev. Phys. Chem., in press). Comparisons of the experimental with the theoretical densities will be made.

06.2-23 THE ELECTRON DENSITY DISTRIBUTION IN HEMATITE,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. By M.Yu. Antipin, R.G. Gerr, M.P. Flügge, V.G. Tsirel'son, Yu. T. Struchkov, R.P. Ozerov, Mendeleev Institute of Chemical Technology, Moscow, Nesmeyanov Institute of Elementoorganic Compounds, Moscow, USSR.

Very pure single crystal was used in experiment giving 5700 reflections up to  $\sin \theta/\lambda = 1.36 \text{ \AA}^{-1}$  measured with a 4-circle diffractometer Y-290 Hilger-Watts. Corrections for thermal diffuse scattering, absorption and secondary isotropic extinction were made. The final set of independent experimental structure factors consisted of 635 values. 324 of them measured at  $\sin \theta/\lambda > 1.0 \text{ \AA}^{-1}$  were used in high-angle scale factor, positional and thermal parameter refinement. The deformation electron density distribution (DEDD) was constructed with reflections measured at  $\sin \theta/\lambda < 0.75 \text{ \AA}^{-1}$ . In the section along the c-axis there was observed a doubled peak of DEDD ( $1.7 \text{ e\AA}^{-3}$ ) between nearest Fe atoms. It can be attributed to a strong covalent bonding. Between the next nearest Fe atoms there are two minima of DEDD ( $-0.4 \text{ e\AA}^{-3}$ ) and three maxima, one of them ( $0.4 \text{ e\AA}^{-3}$ ) is unexpectedly found in the octahedral hole, two others ( $1.4 \text{ e\AA}^{-3}$ ) between Fe atoms and the octahedral hole. Special attention was paid to the difference of DEDD in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and ruby (Doklady Akademii Nauk SSSR, 271, 1178 (1983)). The behaviour described differs from that in ruby. The DEDD maps in the plane of three oxygen atoms are common in hematite and ruby. Calculations of the electric field gradient on the Fe-nucleus were carried out and comparison with  $\delta$ -resonance value was made.

06.2-24 ELECTRON DISTRIBUTION IN GASB. By R. Uno, J. Ishigaki and H. Ozawa, College of Humanities and Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156, Japan.

Intensity of X-ray diffraction from powder sample of GaSb was measured by the step-scanning method. The incident beam of  $\text{CuK}\alpha_1$  was monochromatized by a quartz monochromator and the intensity of  $\text{CuK}\alpha_2$  was reduced to 2% of  $\text{CuK}\alpha_1$ . Separation of difference lines, where  $h+k+l=4n+2$ , from neighbouring strong lines has been done following a profile-fitting method. A profile-function is assumed to be a sum of a Gaussian and a Lorentzian functions. The square of FWHM of the Gaussian function is approximately given as a smooth function of the Bragg angles, from measurements on seven isolated lines. However, other parameters cannot be expressed by a smooth function, so that they are left as fitting parameters. Since the integrated intensity of the profile-function varies so much by a small variation of parameters, the integrated intensity of diffraction lines is obtained by numerical integration of intensity data. The range of integration is assumed to be from  $-6\text{FWHM}$  to  $+6\text{FWHM}$  around the Bragg angle. If the range of integration of two lines overlaps, the numerical integration is carried out over both lines and the total intensity is divided according to the ratio of individual integrated intensities calculated from the fitted profile functions.

As a result of this estimation, intensities of difference lines except 222 are found to be much less than those measured earlier by the constant speed scanning method, reported at the 11th Congress. Thus difficulty in interpretation of the strong difference lines having large scattering vectors has been removed. Electron density in GaSb is investigated by the difference Fourier synthesis. The electron density corresponding to covalent bond between Ga and Sb is found to be higher than the bond between Ga and As in GaAs. (J. Phys. Soc. Jpn. 28(1970) 437).