The charge density in molecules containing S in various bonding environments is being studied at ~85K by X-ray diffraction. Examples will be taken from the analyses of ethane-1,2-bis(methyl)sulfone, H₃C-SO₂-C₂H₅-C₂H₅-SO₂-C₂H₅, in P₃₂ (a) and dithiocarbamide, S-C(=N₂)₂-(NH₂)₂-O-S, in P6 (5), both structures with S=2. Intensities were collected to a limit in (sinθ)/λ<1.27Å⁻¹. Data processing includes corrections for coincidence loss, scan truncation, multiple diffraction, absorption, anomalous dispersion and extinction before averaging. Details on the analyses of errors due to scan truncation and multiple diffraction will be presented along with some results of the analysis. From statistical tests the Laue class of the X-ray data is m3m, and space-group Pn3m (No. 224) was chosen for the analysis. Around the oxygen the maps display a tetrahedral deformation with peaks located on the oxygen site. In addition, there is a 3-fold pattern of excess density close to Cu distributed around the Cu-O axis. Aromatic (3d)⁵ configuration in a tetrahedral environment is expected to be spherical. In the present case, however, the difference Fourier maps around the Fe³⁺ cation on the A site show a large deformation from the spherical distribution: four positive peaks of 1.0 electron/A³ are tetrahedrally located at 0.36 Å from the Fe nucleus on the extension of the Fe-O bonds. This suggests excess charges in the t₂ level, and is probably due to the formation of the Fe-O covalent bonds. The cation on the B site is octahedrally surrounded by six O⁰ anions: the octahedron is trigonally elongated. Six peaks of 0.6 electrons appear on the D-maps; they are along the body-diagonal directions of the octahedron except the trigonal axis, 0.37 Å away from the cation. This shows that the e_g level having the σ character is lower than the e_g level. The charge asphericity might be partly attributed to anharmonic vibrations of atoms. Further refinement is in progress.

The electron density distribution in the title complexes is being studied using the X-N technique. This pair of complexes has been selected because they have unsupported metal-metal bonds which require formal single bonds to satisfy their observed diamagnetism. Recent studies (e.g. M.Eversen, B.Rees, A.Hitschler, Acta Cryst. 35B (1982) 6) show that there is no significant accumulation of charge density between the metal centres in such systems, an interesting result in view of our conceptions of what constitutes a chemical bond. Further, the Cu-Cr bond is longer than that of the Mo analogue, in contrast to the expected pattern of increasing bond length down a group. A similar observation was made in the unsubstituted (Cu₄)₅ complexes (R.D.Adams and F.A.Cotton, Inorg. Chem. Acta, 17 (1973), 135; F.C.Wilson and D.P.Showmaker, J. Chem. Phys., 77 (1957), 809.), and a detailed description of the electron density distribution should provide an interpretation of these observations. It is intended to present some results of this study at the conference.

We thank Dr. D. Mullen for the extensive data measurements and the Deutsche Forschungsgemeinschaft for financial support.

06.2-7 EXPERIMENTAL CHARGE DENSITY IN MOLECULES CONTAINING SULFUR. By F. Mo and G. Thorvaldsen, Institutet for rentgentechnik, Universitetet i Tromsø-NTH, N-7034 Tromsø-NTH, Norway.

The electron density distribution in magnetite was investigated by X-ray diffraction. Single crystals were prepared by the Bridgman method. A crystal shaped into a sphere of 0.286 (4) mm in diameter was used for intensity measurement on an automated four-circle diffractometer with monochromated Ag Kα radiation up to a 2θ value of 150°. In total, 5253 (382 unique) reflections in a hemisphere of the reciprocal space were collected. The structure was refined to F=0.020 by the least-squares method. According to a simple crystal-field model, the d-electron distribution of an atom with the high-spin (3d)⁵ configuration in a tetrahedral environment is expected to be spherical. In the present case, however, the difference Fourier maps around the Fe³⁺ cation on the A site show a large deformation from the spherical distribution: four positive peaks of 1.0 electron/A³ are tetrahedrally located at 0.36 Å from the Fe nucleus on the extension of the Fe-O bonds. This suggests excess charges in the t₂ level, and is probably due to the formation of the Fe-O covalent bonds. The cation on the B site is octahedrally surrounded by six O⁰ anions: the octahedron is trigonally elongated. Six peaks of 0.6 electrons appear on the D-maps; they are along the body-diagonal directions of the octahedron except the trigonal axis, 0.37 Å away from the cation. This shows that the e_g level having the σ character is lower than the e_g level. The charge asphericity might be partly attributed to anharmonic vibrations of atoms. Further refinement is in progress.

06.2-8 ELECTRON-DENSITY DISTRIBUTION IN CRYSTALS OF MAGNETITE AT ROOM TEMPERATURE. By S. Sato and S. Todo, The Institute for Solid State Physics, The University of Tokyo, Roppongi 7-22-1, Hünanto-ku, Tokyo 106, Japan.

The electron density distribution in magnetite was investigated by X-ray diffraction. Single crystals were prepared by the Bridgman method. A crystal shaped into a sphere of 0.286 (4) mm in diameter was used for intensity measurement on an automated four-circle diffractometer with monochromated Ag Kα radiation up to a 2θ value of 150°. In total, 5253 (382 unique) reflections in a hemisphere of the reciprocal space were collected. The structure was refined to F=0.020 by the least-squares method. According to a simple crystal-field model, the d-electron distribution of an atom with the high-spin (3d)⁵ configuration in a tetrahedral environment is expected to be spherical. In the present case, however, the difference Fourier maps around the Fe³⁺ cation on the A site show a large deformation from the spherical distribution: four positive peaks of 1.0 electron/A³ are tetrahedrally located at 0.36 Å from the Fe nucleus on the extension of the Fe-O bonds. This suggests excess charges in the t₂ level, and is probably due to the formation of the Fe-O covalent bonds. The cation on the B site is octahedrally surrounded by six O⁰ anions: the octahedron is trigonally elongated. Six peaks of 0.6 electrons appear on the D-maps; they are along the body-diagonal directions of the octahedron except the trigonal axis, 0.37 Å away from the cation. This shows that the e_g level having the σ character is lower than the e_g level. The charge asphericity might be partly attributed to anharmonic vibrations of atoms. Further refinement is in progress.

06.2-9 ELECTRON-DENSITY DISTRIBUTION IN MOLECULES CONTAINING SULFUR. By F. Mo and G. Thorvaldsen, Institutet for rentgentechnik, Universitetet i Tromsø-NTH, N-7034 Tromsø-NTH, Norway.

The charge density in molecules containing S in various bonding environments is being studied at ~85K by X-ray diffraction. Examples will be taken from the analyses of ethane-1,2-bis(methyl)sulfone, H₃C-SO₂-C₂H₅-C₂H₅-SO₂-C₂H₅, in P₃₂ (a) and dithiocarbamide, S-C(=N₂)₂-(NH₂)₂-O-S, in P6 (5), both structures with S=2. Intensities were collected to a limit in (sinθ)/λ<1.27Å⁻¹. Data processing includes corrections for coincidence loss, scan truncation, multiple diffraction, absorption, anomalous dispersion and extinction before averaging. Details on the analyses of errors due to scan truncation and multiple diffraction will be presented along with some results of the analysis. From statistical tests the Laue class of the X-ray data is m3m, and space-group Pn3m (No. 224) was chosen for the analysis. Around the oxygen the maps display a tetrahedral deformation with peaks located on the oxygen site. In addition, there is a 3-fold pattern of excess density close to Cu distributed around the Cu-O axis. Around the oxygen the maps display a tetrahedral deformation with peaks located on the Cu-O bond 0.62 Å from the oxygen site. This indicates both ionic and covalent contributions to the bonding in cuprite.

Further work on the X-ray data is in progress, supplemented by neutron data collected by D. Mullen (loc. cit.) at 80, 120, 199, and 295 K.

We thank Dr. D. Mullen for the extensive data measurements and the Deutsche Forschungsgemeinschaft for financial support.