06.3–13 NON-LOCAL ELECTRON-ELECTRON CORRELATION EFFECTS IN THE MOMENTUM DENSITY OF COPPER METAL. By G.E.W. Bauer and J.R. Schneider, Hahn-Meitner-Institut für Kernforschung, Berlin (FRG).

The <110> directional total Compton profile of copper has been measured with high accuracy by 412 keV γ-ray scattering with special care for the multiple scattering correction. The results complete and are consistent with earlier measurements of Compton profile anisotropies and the long range part of the one-electron autocorrelation function $B(\vec{r})$ (Pattison, Hansen & Schneider, Z.Physik B(1982)46,285). By tight-binding model calculations the observed structures in the Compton profiles can be explained qualitatively by hybridization and orthogonalization effects between plane waves and d-orbitals. However, the difference between existing first-principles band structure calculations in the density-functional formalism and the experiment is probably not due to an incorrect description of orthogonalization and hybridization (Bauer & Schneider, Z.Phys.B (1983)54,17).

A correlation correction funtional which is required for a rigorous calculation of momentum densities in the density-functional formalism is calculated in the local-density approximation (Bauer, Phys.Rev.B(1983)27,5912). The agreement between experiment and theory for the <110> Compton profile is improved, but significant oscillations remain unexplained, which are also responsible for the discrepancies in the anisotropies. The periodicity of the observed non-local correlation effects can be characterized by the topology of the copper Fermi surface in the extended zone scheme. We believe that the observations can be explained by short lived resonances at lower binding energies. The results also shed some light on the origin of the success of the local-density approximation: By the virial theorem the non-local part of the exchange-correlation energy functional is obtained by a simple integration of the difference between the full local-density-functional calculation and the experimental total Compton profile. Since the observed oscillations cancel to a large extent in this integration, the non-local contribution must be small.

06.4–1 ON THE $3d^5$ ELECTRON SHELL DEFORMATION OF Fe^{3+} IONS IN SPINEL STRUCTURES. By S. Ligenza, Institute of Atomic Energy, Laboratory of Solid State Physics, 05-400 Świerk, Poland.

Deformation of the $3d^5$ electron shell of Fe^{3+} ions in some spinel ferrites was observed by neutron spectroscopy (NS) (Ligenza, phys. stat. sol. (1976) 75,315 and (1978) 86,635). In order to obtain the complementary information, the Mössbauer effect (ME) studies have also been performed (Ligenza et al., phys. stat. sol. (1981) 105,350 and (1983) 117,465). Basing on the NS and ME results the analysis of the deformation mechanism is given. It was found that the deformation is caused by the following effects:

(i) The presence of some covalency processes bringing about a decrease of charge density $\Delta\delta$ at the $|z^2\rangle$, $|xz\rangle$ and $|yz\rangle$ orbitals relative to the $|x^2-y^2\rangle$ and $|xy\rangle$ ones. This deformation may be called an "electron deformation".

(ii) The increase of the radial distribution $\Delta\rho$ of the $|xy\rangle$ and $|x^2-y^2\rangle$ orbitals relative to the $|z^2\rangle$, $|xz\rangle$ and $|yz\rangle$ ones gives the deformation which may be called a "geometrical deformation". Taking into account the quadrupole parameter D= -0.61 meV and the quadrupole shift $\varepsilon(3d)$ = -0.040 mm/s for manganese ferrite and assuming the electric field gradient at B-sites equal to the one determined in ME measurements, the electron deformation was found to be $\Delta\delta$=-0.067 whereas the geometrical deformation was $\Delta\rho$= +0.027. The above deformation for zinc ferrite is $\Delta\delta$=-0.089 and $\Delta\rho$=+0.035 for D=-0.67 meV and $\varepsilon(3d)$ =0.030 mm/s.

06.4–2 CHEMICAL PROPERTIES FROM THE PROMOLECULE. By M. Spackman and E.N. Maslen, Department of Physics, University of Western Australia.

Considerable effort is expended on accurate measurements of deformation densities, in order to improve our understanding of the properties of materials. The chemical information contained in the electron density for the promolecule – an assembly of undeformed atoms at the equilibrium positions – is not always recognised.

Subdivision of the promolecule into virial fragments (R.F.W. Bader and P.M. Beddall, J.A.C.S., 95, 305 (1973) gives a convenient model for studying these properties. Atomic radii derived from the fragments are characteristic of chemical bonding. In homonuclear diatomics the radii are, axiomatically, those for uncharged atoms. For heteronuclear diatomics consisting of electronegative and electropositive atoms the radii are typical of ionic bonding although there is no transfer of charge in the promolecule. The atomic radii for polyatomic species are determined by the atomic densities and the contact distances, being minimally affected by contributions to the density from more distant atoms.

There is strong correlation between the electrostatic energy (estimated from effective nuclear charges derived within spheres of radii defined by the atomic model) and the dissociation energy for diatomic molecules, which is also affected by the electronegativities of the bonded atoms. Electronegativity may thus be related to the effective nuclear charge in the valence shell.

Since virial partitioning defines pseudo-atom boundaries, it divides the deformation density into regions which, when integrated, yield atomic charges. The boundaries of the virial fragments are changed by the deformation of the density, but charges from promolecule fragments are a reasonable approximation to those from molecular densities.