06.2-19 THE ELECTRON DENSITY IN METALS AND SEMI-CONDUCTORS USING ELECTRON AND X-RAY DIFFRACTION.

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Difference charge density maps for Si, Ge, Cu, Al, Fe and Ni have been constructed using a combination of (a) electron diffraction and X-ray diffraction measurements or (b) electron diffraction measurements and band theory calculations. The distributions are significantly more detailed, and we believe more precise, than those obtain-ed previously. The maps show various new features which relate to physical properties.

For Si and Ge, electron diffraction critical voltage measurements have been used for the low order structure factors, and X-ray diffraction results for the higher order. The spatial location of the valence electrons is highlighted by plotting the valence charge density, a difference charge density defined as

$$\rho_{val}(\underline{r}) = \frac{1}{\Omega}\sum_g [F_g^x(\text{cryst}) - F_g^x(\text{ion})]\exp(2\pi i\underline{g}\cdot\underline{r})$$

where Ω is the unit cell volume, F_g^x(cryst) is the observed X-ray structure factor for the reflection g for the crystal and F_g^x(ion) is the calculated free ion structure factor, in this case for Si^{4+} and Ge^{4+}. Observed values of the electron structure amplitude, determined from critical voltage effect measurements, were converted to the corresponding X-ray structure factor, F_g^x(cryst), using the Mott formula. Maps of the valence charge density reveal that the valence bond shape for both Si and Ge is approximately cylindrical, with the cylinder axis along the nearest neighbour direction. This is consistent with the usual sp^3 hybrid orbital model being an approximation which is improved by the addition of some d and f character, as proposed by Pauling.

The spatial redistribution of the atomic electrons which occurs due to bonding is highlighted by the deformation charge density, a difference charge density defined as

$$\Delta\rho(\underline{r}) = \frac{1}{\Omega}\sum_g [F_g^x(\text{cryst}) - F_g^x(\text{atom})]\exp(2\pi i\underline{g}\cdot\underline{r})$$

where F_g^x(atom) is the calculated X-ray structure factor for free atoms. Maps of the deformation charge density for Si and Ge reveal that electrons are more severely depleted from the atomic sites and the depletion extends over a much larger region in Ge than in Si. This is consistent with the higher substitutional solubility of many of the larger impurity atoms in Ge than in Si. In both Si and Ge, electrons are slightly depleted from the largest interstitial sites in the structure. At the high level of accuracy of these electron density maps the dominant source of error is the uncertainty in the anomalous dispersion correction for the observed X-ray structure factors. The major effect of this uncertainty takes place in the region of the atomic sites and provided that one is interested only in the bond region then the uncertainty in anomalous dispersion is not too serious.

In Cu, unlike Si and Ge, the difference density maps show there is no build up of charge in the nearest neighbour direction, and there is a concentration of conduction electrons in both the tetrahedral and octahedral interstitial sites. This is consistent with the observation that self-interstitials in copper do not occupy the tetrahedral or octahedral sites but have a [100] split interstitial configuration at precisely the points shown on our map to have a deficit of electrons. In Fe, the <100> directions are easy directions of magnetization while <111> are hard. Ni has easy directions along <111> and hard along <100>. Our density maps exhibit the corresponding asymmetries.

06.2-20 THE DEFORMATION ELECTRON DENSITY IN SULFATES, CHLORATES AND SILICATES.

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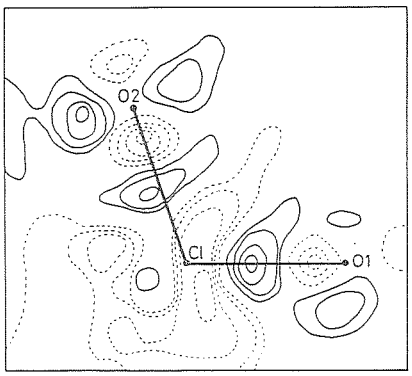
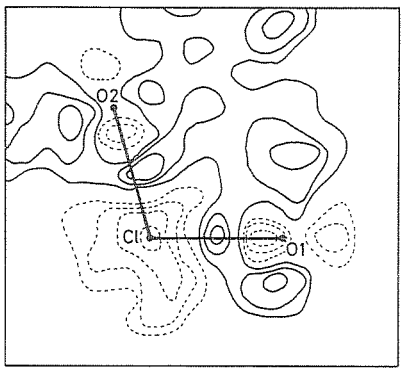
In our laboratory electron density studies are being performed on sulfates, chlorates and silicates. So far work is in progress on the following compounds : $KClO_4$, $KClO_3$, $Na_2S_2O_3$, $MgS_2O_3\cdot 6H_2O$ and α-Fe_2SiO_4 (synthetic fayalite). All these compounds have been studied by a combination of accurate X-ray and neutron diffraction measurements at 120K.

The general features of the deformation density in the various compounds is rather similar. Peak heights of 0.3 to 0.6 $e\text{Å}^{-3}$ are found in the Cl-O, S-O, S-S and Si-O bonds. Lone pair peaks at the oxygen atoms are observed in all compounds at angles of about 100° with the bond axes. No lone pair density is observed at the apex of the Cl atom in $KClO_3$. The dominant features in α-Fe_2SiO_4 are two peaks of 1.0 to 1.2$e\text{Å}^{-3}$ at opposite sites of the Fe atoms. They occur for both independent Fe atoms and are similar to the peaks observed in γ-Fe_2SiO_4 (Marumo et al., Acta Cryst. B33 (1977) 713). They are believed to result from a non-spherical distribution of d-electrons.



X-N deformation density in $KClO_4$

Contour interval 0.1 $e/\text{Å}^{-3}$, zero contour omitted.

Preliminary X-N deformation density in $KClO_3$