
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 of (b) electrons. This has been compared with theoretical calculations. The distributions are significantly more detailed, and we believe more precise, than those obtained 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

\[
p_{\text{val}}(z) = \frac{1}{N} \sum_{g} \left( F_{g}^{(\text{cryst})} - F_{g}^{(\text{ion})} \right) \exp(2\pi i g \cdot z)
\]

where \( z \) is the unit cell volume, \( F_{g}^{(\text{cryst})} \) is the observed X-ray structure factor for the reflection \( g \) for the crystal and \( F_{g}^{(\text{ion})} \) is the calculated free ion structure factor, in this case for Si \( ^{26} \) and Ge \( ^{28} \). Observed values of the electron structure amplitude, determined from critical voltage effect measurements, were converted to the corresponding X-ray structure factor, \( F_{g}^{(\text{cryst})} \), using the Nott 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

\[
\delta p(z) = \frac{1}{N} \sum_{g} \left( P_{g}^{(\text{cryst})} - P_{g}^{(\text{atom})} \right) \exp(2\pi i g \cdot z)
\]

where \( P_{g}^{(\text{cryst})} \) 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 substitutability 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 tetrahedral and octahedral structures. 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 conductive 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 <110> and hard along <100>. Our density maps exhibit the corresponding asymmetries.