Electric field gradients have been measured at substitutional lattice sites in ternary semiconductors using Perturbed Angular Correlation spectroscopy (PAC). The experimental results for $\text{A}^{I}\text{B}^{II}\text{C}^{VI}$ chalcopyrite structure compounds and $\Box\text{A}^{II}\text{B}^{IV}\text{C}^{VI}$ defect chalcopyrites are compared with ab-initio calculations. The latter were carried out with the WIEN code that uses the Full Potential Linearized Augmented Plane Wave method within a density functional theory. The agreement between experiment and theory is in most cases very good. Furthermore, the anion displacements in AgGaX$_2$-compounds ($X$: S, Se, Te) have been determined theoretically by determining the minimum of the total energy of the electrons in an elementary cell.

**Key words:** Quadrupole Interaction; Chalcopyrite Semiconductors; First Principles Calculations; Perturbed Angular Correlations; Structure Parameters.