# Quadrupole Interaction in Ternary Chalcopyrite Semiconductors: Experiments and Theory

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Electric field gradients have been measured at substitutional lattice sites in ternary semiconductors using Perturbed $\gamma$-$\gamma$ Angular Correlation spectroscopy (PAC). The experimental results for $A^{I}B^{III}C_2^{VI}$ chalcopyrite structure compounds and $\square A^{II}B_2^{III}C_4^{VI}$ 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.

## Introduction

An enormous progress in the theoretical treatment of electric charge density distributions and electric field gradients (efg) in solids has been achieved within the last years. Thus quadrupole coupling constants and therefore efg determined experimentally via hyperfine interactions obtain an increased importance for ab-initio calculated charge distributions in solids. In this work, experiments were performed using PAC spectroscopy (Perturbed Angular Correlation of successive $\gamma$-quanta). The ISOLDE on-line mass separator at CERN has been used for the production of suitable PAC probes and their implantation into ternary semiconductors. It is possible to substitute up to five different lattice sites in the compounds investigated by PAC probes. We have computed the corresponding efg at regular lattice sites in ternary chalcopyrite structure semiconductors with the WIEN 95/97 code [1]. The results for two classes of compounds, $A^{I}B^{III}C_2^{VI}$ chalcopyrite structure semiconductors and $\square A^{II}B_2^{III}C_4^{VI}$ defect chalcopyrites, are discussed in this work.

$A^{I}B^{III}C_2^{VI}$ compounds can be derived from $A^{II}B^{VI}$ semiconductors if the divalent cations are substituted by equal numbers of mono- and trivalent atoms. Thereby the crystal symmetry is reduced. Most of these compounds crystallize in the chalcopyrite structure which is characterized by the tetragonal compression $\tau = 2 - c/a$ and the anion displacement $\sigma = x - 1/4$ ($x$ = relative anion position). The experimental determination of $\sigma$ is difficult. That is why a theoretical approach has been chosen.

$\square A^{II}B_2^{III}C_4^{VI}$ semiconductors can be obtained from the $A^{I}B^{III}C_2^{VI}$ chalcopyrite compounds by substitution of half of the atoms at A-sites by divalent atoms and leaving the other half sites unoccupied. As a consequence, the anions relax towards the vacancy in three lattice directions and two non-equivalent B-sites can be distinguished. Up to four efg values per

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Table 1. Largest components $V_{zz}$ of the efg in units of $10^{21}$ V/m$^2$ at different lattice sites in the chalcopyrite structure semiconductors $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$ and $CuInSe_2$. The point symmetry at the cation sites is the reason for axial symmetry of the efg, i. e. $\eta = 0$. An asymmetry parameter is given only for the C-site. The references for the lattice parameters $a$ and $c$ are given with the compound. The theoretically determined anion displacement has been used for the Ag-compounds. The uncertainties of the quadrupole moments are smaller than 16% [7] and were not included into the experimentally determined efg values. ($^{63}$Cu, $^{115}$In [8]; $^{69}$Ga [9]; $^{111m}$Cd in $AgGaTe_2$ and $^{111}$Ag($^{111}$Cd) this work; other experimental values [10]).

| $A^IB^{III}C_2^{VI}$ | | $\tau$ | — A-site — | | | — B-site — | | | — C-site — | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Experiment | | Theory | Experiment | | Theory | Experiment | | Theory |
| $AgGaS_2$ | [4] | 0.211 | $^{111m}$Cd | | | $^{111}$In($^{111}$Cd) | 0.29 | | | | –8.1 |
| | | | $^{111}$Ag($^{111}$Cd) | +5.7 | +5.0 | $^{69}$Ga | 0.10 | +0.40 | | | $\eta = 0.78$ |
| $AgGaSe_2$ | [5] | 0.207 | $^{111m}$Cd | 4.6 | +4.6 | $^{111}$In($^{111}$Cd) | 0.28 | | $^{77}$Br($^{77}$Se) | 16 | –17.5 |
| | | | | | | $^{69}$Ga | 0.14 | +0.58 | | $\eta = 0.86$ | $\eta = 0.72$ |
| $AgGaTe_2$ | [6] | 0.103 | $^{111m}$Cd | 2.4 | +2.4 | | | +0.16 | | | –27.4 |
| | | | | | | | | | | | $\eta = 0.76$ |
| $CuInSe_2$ | [5] | 0.035 | $^{63}$Cu | 0.15 | +0.09 | $^{115}$In | 0.10 | +0.32 | $^{77}$Br($^{77}$Se) | 14.6 | –14.8 |
| | | | | | | | | | | $\eta = 0.39$ | $\eta = 0.58$ |

substance can be used to compare theory and experiment.

## Experimental

In chalcopyrite compounds, electric field gradients (efg) are present at lattice sites because of the non-cubic point symmetry. The experiment gives the quadrupole coupling constant $\nu_Q$ and the asymmetry parameter $\eta$ of the efg. The largest component $V_{zz}$ of the efg is directly proportional to the quadrupole coupling constant: $V_{zz} = h\nu_Q/(eQ)$ ($h$ = Planck's constant, $e$ = elementary charge, $Q$ = quadrupole moment). $\gamma$-$\gamma$ PAC measurements have been performed with a standard 4-detector setup using $BaF_2$ or NaI(Tl) scintillation detectors. In addition, $\beta$-$\gamma$ PAC measurements allow to determine the sign of $V_{zz}$. They have been carried out using two $BaF_2$-scintillation detectors for $\gamma$-quanta at an angle of 90° in the horizontal plane and one plastic scintillation detector for $\beta$-particles emitted by $^{111}$Ag above the single crystalline sample. The crystals have been provided by E. Treser, V. Krämer (Universität Freiburg i. Br.), A. Chevy, M. May (Université Pierre et Marie Curie, Paris), N. A. Moldovyan and I. M. Tiginyanu (Academy of Sciences of Moldova).

The PAC probes $^{77}$Br($^{77}$Se), $^{111m}$Cd, $^{111}$In($^{111}$Cd), $^{111}$Ag($^{111}$Cd), $^{117}$Cd($^{117}$In), and $^{199m}$Hg were implanted with an energy of 60 keV (350 keV for $^{111}$In($^{111}$Cd)) into the substances investigated. After implantation the samples were sealed in evacuated quartz ampoules in order to avoid oxidation during thermal annealing of radiation damages.

## Theoretical Approach

The WIEN95/97 code [1] applies the Full Potential Linearized Augmented Plane Wave method (FLAPW). The charge density distribution in an elementary cell is calculated self consistently from first principles within a density functional approach. Since the charge density distribution determines the electrical potential, the efg tensors can be calculated at lattice sites as its second derivatives.

In order to calculate the efg in the cases of impurity probes, e. g. $^{111m}$Cd substituting Hg in $HgGa_2Se_4$, it would be necessary to create a supercell consisting of 8 unit cells. One Hg atom in this super cell had to be substituted by a Cd atom. The calculation would then give the efg at the impurity position in the supercell. Such calculations could not be carried out up to now because of their enormous need of computational power for taking into account such a large number of atoms in the supercell.

That is why a Sternheimer correction has been applied to the efg experimentally determined in order to compare them with theoretical results in the cases of impurity probes. For $^{111m}$Cd substituting Hg in $HgGa_2Se_4$ the largest component of the efg at the Hg-site is calculated as $V_{zz,\mathrm{Hg}} = \left((1-\gamma_\infty)_{\mathrm{Hg}}/(1-\gamma_\infty)_{\mathrm{Cd}}\right)V_{zz,\mathrm{Cd}}$ ($V_{zz,\mathrm{X}}$ = largest component of efg observed with atom X at a certain lattice site, $(1-\gamma_\infty)_{\mathrm{X}}$= Sternheimer factor for an ion of element X [2]). The

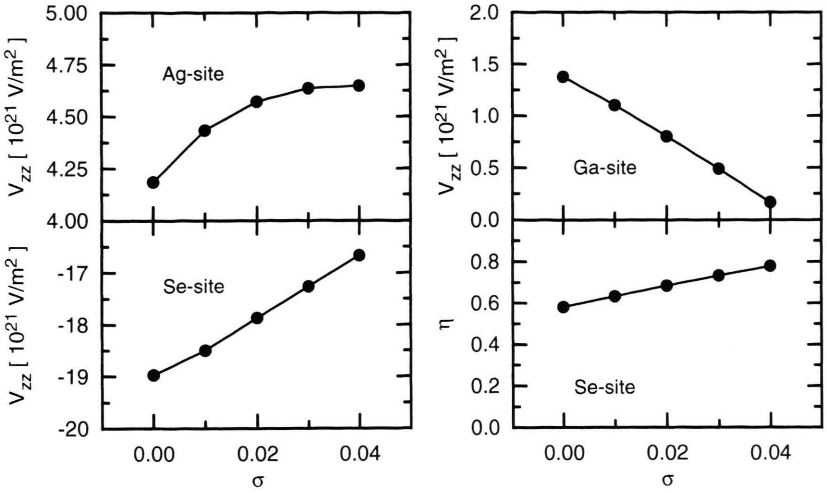

Fig. 1. Largest component $V_{zz}$ of the efg in units of $10^{21}$ V/m$^2$ calculated with WIEN97 for $AgGaSe_2$ in dependence on the anion displacement $\sigma$: Ag-site (top left), Ga-site (top right), Se-site (bottom left). The values of the asymmetry parameter $\eta$ are drawn on the bottom right.

shortcomings of such considerations are well known. Nevertheless, the possible uncertainty in the quotient is much smaller than that of a single multiplier.

## Results and Discussion

### *$A^IB^{III}C_2^{VI}$-Compounds*

Both the experimentally and theoretically estimated values of the largest component $V_{zz}$ of the efg and the asymmetry parameter $\eta$ for all studied compounds are given in Table 1. The agreement between experiment and theory turns out to be very good for the A- and C-sites. $\beta$-$\gamma$ PAC measurements have been carried out using $^{111}Ag(^{111}Cd)$ in $AgGaS_2$. This way the theoretically determined sign of an efg has been verified in one case.

The size of the efg at B-sites is relatively low because of the relative small distortion of the tetrahedra formed by next nearest neighbours. Theory does not reproduce the B-site efg very well, not even in the cases of NMR experiments using the host atoms $^{115}In$ in $CuInSe_2$ and $^{69}Ga$ in $AgGaS_2$ and $AgGaSe_2$. The theoretical values are roughly four times larger than the NMR results. The PAC data are found in between.

Difficulties in the theoretical determination of B-site efg have been explained with help of point charge model calculations. The B-site efg is the difference of two large contributions with nearly the same value [3]. Consequently, the difference has a much higher relative uncertainty than these two contributions.

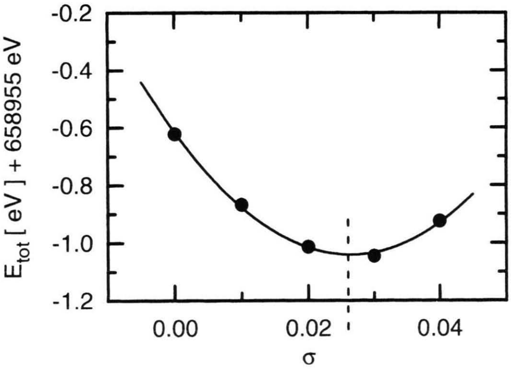

Fig. 2. Total energy $E_{tot}$ calculated for different values of the anion displacement $\sigma$ for $AgGaSe_2$. The dashed line marks the experimental value [5]. The solid line represents a quadratic fit.

Table 2. Experimental and theoretical anion parameters $\sigma$ of chalcopyrite structure compounds.

| | — σ — | | |
|---|---|---|---|
| | — Theory — | | |
| Substance | [11] | This work | Experimental |
| $AgGaS_2$ | | 0.032 | 0.0408(4) |
| $AgGaSe_2$ | 0.045 | 0.027 | 0.026(3) |
| $AgGaTe_2$ | | 0.016 | 0.01 |

The calculations show that the B-site efg depends much stronger on the anion parameter $\sigma$ than the efg at other positions. As an example, the results for $AgGaSe_2$ are drawn in Figure 1. It is difficult to determine the anion parameter from X-ray diffraction experiments precisely since not only the line positions but also their intensities have to be examined accurately. Therefore a theoretical determination of the anion displacement has been carried out for the Ag-compounds. The total energy of the electrons in an elementary cell was calculated for fixed lattice

Table 3. Largest component $V_{zz}$ of the efg in units of $10^{21}$ V/m$^2$ measured in defect chalcopyrite compounds and calculated with WIEN95/97. The calculations give axially symmetric efg for the cation sites. The asymmetry parameters for the anion sites are tabulated. The values for $CdAl_2S_4$ and $CdGa_2Se_4$ have been taken from [19], except for the one measured with $^{117}$Cd($^{117}$In). The results for $^{71}$Ga have been measured by NMR [20].

| | | | — A-site — | | | — B(1)-site — | | | — B(2)-site — | | | — C-site — | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\tau$ | Exp. | | Theory | Exp. | | Theory | Exp. | | Theory | Exp. | | Theory |
| $HgGa_2Se_4$ | [15] | 0.09 | $^{199m}$Hg | 3.5 | +3.5 | $^{111}$In($^{111}$Cd) | 1.5 | −1.2 | $^{111}$In($^{111}$Cd) | 1.6 | +1.4 | $^{77}$Br($^{77}$Se) | 28(4) | −17.0 |
| | | | $^{111m}$Cd | 3.6 | | | | | | | | | $\eta = 0.2(1)$ | $\eta = 0.44$ |
| $CdGa_2Se_4$ | [16] | 0.13 | $^{111m}$Cd | 2.0 | +2.0 | $^{111}$In($^{111}$Cd) | 1.2 | −1.1 | $^{111}$In($^{111}$Cd) | 1.5 | +1.7 | $^{77}$Br($^{77}$Se) | 13.4 | −16.9 |
| | | | $^{117}$Cd($^{117}$In) | 3.6 | | | | | | | | | $\eta = 0.61$ | $\eta = 0.68$ |
| $CdGa_2S_4$ | [17] | 0.17 | $^{111m}$Cd | 3.3 | +2.4 | $^{71}$Ga | 1.0 | +0.24 | $^{71}$Ga | 1.8 | +1.7 | | | −9.6 |
| | | | | | | $^{111}$In($^{111}$Cd) | 1.2 | | $^{111}$In($^{111}$Cd) | 1.5 | | | | $\eta = 0.58$ |
| $CdAl_2S_4$ | [18] | 0.18 | $^{111m}$Cd | 3.9 | +4.0 | $^{111}$In($^{111}$Cd) | 0.29 | −0.29 | $^{111}$In($^{111}$Cd) | 0.34 | +0.42 | | | −6.6 |
| | | | | | | | | | | | | | | $\eta = 0.22$ |

parameters $a$ and $c$ and different anion displacements. The dependence of the total energy on the anion parameter $\sigma$ is drawn for $AgGaSe_2$ in Figure 2.

The fit to the calculations with a quadratic dependence on $\sigma$ gives the minimum of the total energy for an anion displacement of $\sigma = 0.027$. This equals the experimental value of $\sigma = 0.026(3)$ [5]. Experimentally determined anion parameters $\sigma$ are given in Table 2 for comparison with a theoretically determined one ($AgGaSe_2$) from [11] and the anion displacements determined in this work. The anion parameter from [11] is nearly twice as large as both the experimentally determined one and the value calculated in this work.

### □$A^{II}B_2^{III}C_4^{VI}$-*Defect Chalcopyrites*

Calculations of efg using the code WIEN95 were also carried out for defect chalcopyrites. Both experimental and theoretical values from the literature and this work are compared in Table 3. In defect chalcopyrites, the B-site efg are larger than in the chalcopyrite structure compounds and are of the same order of magnitude as the A-site efg. That is due to the relatively large deformation of the tetrahedra formed by next nearest neighbours.

The agreement of theory and experiment is very good for the cation sites in most cases. Discrepancies of more than 20% are found for the Se-site in the mercury compound and for the A- and B(1)-sites in $CdGa_2S_4$. The measurement with $^{117}$Cd($^{117}$In) in $CdGa_2Se_4$ gives a relatively large efg.

The Sternheimer correction has been carried out using values of antishielding factors in crystals [12], mostly. In the cases of Hg and In, the values have been used for a free ion [2] and an atom [13], respectively.

The method of calculating efg for ideal crystals and correcting impurity cases using the Sternheimer antishielding factor works very well for the ternary semiconductors investigated in this work. One general hint is the good agreement between experimental and theoretical values of efg. Even more indications have been given in the cases of the A-site efg in $HgGa_2Se_4$ and $CdGa_2Se_4$ and the two B-site efg in $CdGa_2S_4$. For these sites, there exist measurements both with a host atom probe and an impurity probe. The correspondence between the experimentally determined efg with atoms of two different elements is very good in three out of four examples. So, the use of Sternheimer correction is well founded. This is known from the literature for binary wurtzite-type semiconductors [14], too.

Possible sources of errors are the anion parameters like in the case of chalcopyrite type substances. These uncertainties could effect the A- and B-site efg. The C-site efg are relatively large because of the nonsymmetric occupation of the tetrahedron of next neighbours by one A-, two B-atoms and a vacancy. This leads furthermore to the observation that the C-site efg are rather insensitive to changes in the anion parameters. A determination of anion parameters by minimizing the total energy is impossible at present. The anion displacements would have to be taken into account in three directions. Such calculations require a high computational power.

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