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## Monoclinic and orthorhombic cysteine crystals are small gap insulators

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## ABSTRACT

The electronic band structure of both the monoclinic and orthorhombic cysteine polymorphs is investigated using density functional theory (DFT) calculations in the generalized gradient approximation (GGA). Besides, orthorhombic cysteine crystals were grown, and their optical absorption was measured, being estimated an energy gap of  $E_g^{exp} = 4.68$  eV for recrystallized cysteine powder. The existence of a small secondary optical absorption structure for the recrystallized sample around 4.4 eV suggests the existence of defect levels inside the band gap. The calculated valence and conduction bands are very flat for both cysteine polymorphs, suggesting that they are insulators.

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Molecular crystals formed from the nucleotide bases (guanine, adenine, cytosine, thymine) [1] or amino acids (there are 20 natural) [2,3] are interesting structures. There are efforts to take advantage of them for the development of biosensors and optoelectronic devices [4]. Recently, it was demonstrated that anhydrous crystals of DNA bases are wide gap semiconductors [1]; in the case of amino acid crystals, only few were investigated, with results suggesting that alanine, leucine, isoleucine, and glycine [2,3,5] are wide band gap semiconductors, while valine could be a small band gap insulator [2].

The character of charge transport in cysteine crystals is investigated in this work. L-Cysteine, the 2-amino-3-thiol propane carboxylic acid, chemical formula  $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$ , is one of the most important amino acids. As demonstrated by X-ray diffraction and neutron scattering [6–9], L-cysteine has monoclinic and orthorhombic polymorphs, the latter being the dominant phase in high purity powder samples, with small amounts of the DL-cysteine and the monoclinic L-cysteine present as impurities [10]. Optical absorption measurements are performed here only on the orthorhombic cysteine crystals due to its higher stability. By taking advantage of the X-ray diffraction and neutron scattering data of both cysteine polymorphs [6–9], calculations of the structural

and electronic properties are performed within the scope of the density functional theory (DFT) using the generalized gradient approximation (GGA).

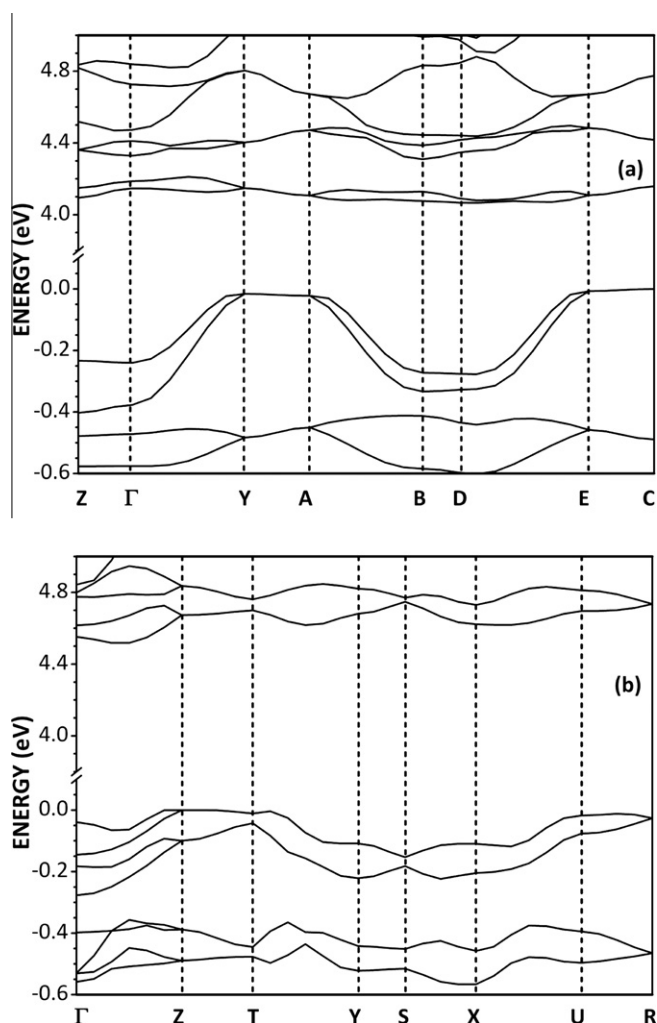
The computational simulations were carried out using the CASTEP code [11,12], which is based in the DFT approach [13,14]. The generalized gradient approximation (GGA), through the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE) [15], was adopted. Norm-conserving pseudopotentials were used to describe the core electronic states of each atomic species [16], and the Kohn–Sham orbitals were evaluated using a plane wave basis set with a converged energy cutoff of 980 eV. Each unit cell was relaxed to attain a total energy minimum allowing for lattice parameter and atomic position adjustments. Convergence thresholds selected for the geometry optimization were: total energy variation smaller than  $2.0 \times 10^{-9}$  eV/atom, maximum force per atom smaller than 0.01 eV/Å, maximum displacement smaller than  $5.1 \times 10^{-4}$  Å, and maximum stress component smaller than 0.05 GPa. A two step convergence window was employed together with the BFGS minimizer [17]. The basis set quality was kept fixed despite the changes of the unit cell volume which occur during the geometry optimization process. The self-consistent field steps have taken into account tolerances of  $5.0 \times 10^{-7}$  eV/atom for total energy and  $0.498 \times 10^{-6}$  eV for the electronic eigenenergies. From the valence band (VB) and conduction band (CB) curves at their critical points (maxima for VB and minima for CB) the effective masses for electrons and holes for the cysteine polymorphs can be estimated, being directly related to the flatness degree of the bands at critical points.

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The crystal lattice parameters and atomic positions used as inputs for the calculations were taken from X-ray diffraction and neutron scattering data already published for the monoclinic and orthorhombic cysteine crystals [6–9]. The asymmetric unit of monoclinic cysteine has two crystallographically independent molecules, *l*-Cys (A) and *l*-Cys (B). On the other hand, the orthorhombic form has the thiol H atom disordered over two sites, forming alternate interactions with either a carboxylate O atom or the S atom of another thiol group [9]. To estimate the hydrogen atomic positions in the orthorhombic unit cell, the S–H bond length was considered as 1.31 Å and C<sub>3</sub>–S–H was allowed to rotate longitudinal and meridionally generating 189 configurations. Among several relative energy minima, the absolute one was chosen and its related molecular configuration has determined the orthorhombic unit cell atomic arrangement. It was obtained that the GGA–PBE calculated formation energy of the monoclinic and orthorhombic cysteine polymorphs is –103.50 and –105.41 kcal/mol, respectively, suggesting that the former is less stable than the later. The converged unit cell parameters for monoclinic (orthorhombic) cysteine are  $a = 9.453$  Å,  $b = 5.192$  Å,  $c = 11.429$  Å,  $\beta = 108.059^\circ$  ( $a = 7.993$  Å,  $b = 12.246$  Å,  $c = 5.432$  Å), being in good agreement with the X-ray diffraction data [6–9]  $a = 9.441$  Å,  $b = 5.222$  Å,  $c = 11.337$  Å,  $\beta = 109^\circ$  ( $a = 8.116$  Å,  $b = 12.185$  Å,  $c = 5.426$  Å).

The Kohn–Sham electronic band structures of the monoclinic and orthorhombic cysteine polymorphs are shown in Figure 1a

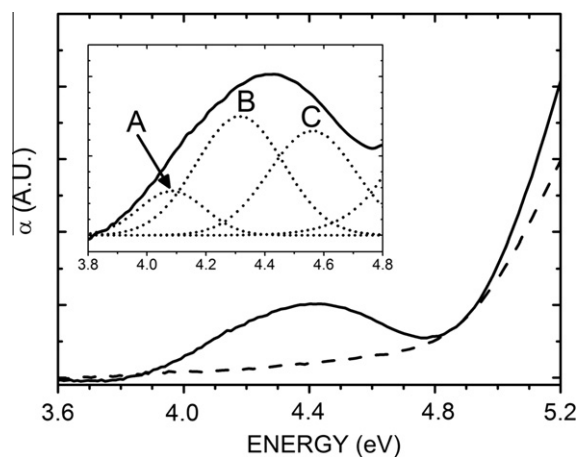


**Figure 1.** Band structure of the cysteine polymorphs: (a) monoclinic and (b) orthorhombic.

and b, respectively. One can observe that both are indirect band gap materials, the former with transition energies D → E of 4.06 eV and A → B of 4.08 eV, and the later with transition energies Z → T, T → Y, and G → Z of 4.52 eV. Previously it was obtained that other amino acid crystals like those of alanine, leucine, isoleucine, valine [2] with  $E_g \sim 5.0$  eV, and glycine with  $E_g \sim 4.6$  eV [3,5] are also wide band gap materials. Due to the flatness degree of their bands at critical points, alanine (orthorhombic), leucine, isoleucine and glycine (monoclinic) were suggested in previous works to be wide band gap semiconductors [2,3,5]. However, the calculated band dispersion flatness at critical points (see Figure 1) suggests that both cysteine polymorphs have insulator characteristics (as in the case of monoclinic valine [2]), which severely limit their use in charge transport applications.

We also have performed optical absorption measurements to estimate the energy band gap of the orthorhombic cysteine polymorph (the most stable one). Cysteine powder samples (sample C1) with at least 99% purity were purchased from Sigma–Aldrich and used with no further purification to grow cysteine crystals by the standard slow evaporation method of recrystallization using deionized water as solvent. The grown crystals were determined to be orthorhombic through X-ray diffraction (data not presented here). The orthorhombic cysteine recrystallized samples were then used to obtain a more purified orthorhombic cysteine powder (C2). The C1 and C2 powders were mixed separately with KBr to form pellets. Light absorption measurements were carried out in the C1–KBr and C2–KBr pellets using a Varian Cary 5000 UV–visible NIR spectrophotometer equipped with solid sample holders. The absorption spectra of the samples were recorded in the 200–800 nm wavelength range (6.21–1.55 eV). The optical absorption measurements were performed by transmittance, with background removal and baseline corrections being made when necessary.

The onset of the absorption coefficient  $\alpha$  as a function of the energy in an indirect gap crystal is related to the incident photon energy by  $\alpha = C(h\nu - E_g \mp \hbar\Omega)^{1/2}$ , where  $C$  is a constant,  $E_g$  is the indirect band gap and  $\mp\hbar\Omega$  is the energy of the absorbed or emitted phonon [19,20]. The spectra for the optical absorption of the C1–KBr (dashed line) and C2–KBr (solid line) pellets are depicted in Figure 2. A weak absorption structure centered around 4.4 eV is observed only in the case of the C2–KBr samples, indicating they are due to the recrystallization process (a similar structure is observed in the case of *l*-alanine crystals obtained in a similar fash-



**Figure 2.** Measured optical absorption of cysteine–KBr pellets made from the original Sigma–Aldrich cysteine powder C1 (dashed line), and the recrystallized cysteine powder C2 (solid line). In the main (stronger) absorption band. The inset shows the deconvolution of the defects related weak C2 band around 4.4 eV, with peak maxima suggesting inside gap defect energy levels roughly at 4.08 eV (A), 4.32 eV (B), and 4.57 eV (C).

ion [18]). One can observe a pronounced absorbance increase beginning around 4.9 eV. In the region where the light absorption of the cysteine–KBr pellets increases strongly, we have estimated the indirect band gap by carrying out a linear fit of the square root of the absorbance, finding a transition energy of 4.62 eV in the case of C1–KBr pellets. On the other hand, the energy gap measured in C2–KBr pellets was estimated at 4.68 eV. The pronounced absorption increase is explained as due to phonon mediated  $Z \rightarrow T$ ,  $T \rightarrow Y$ , and  $G \rightarrow Z$  valence to conduction band electron transfer through the energy gap. As a matter of fact, the measured energy gap of 4.68 eV for C2–KBr pellets is larger than the DFT–GGA calculated energy gap,  $E_g^{calc.} \sim 4.52$  eV, as expected due to the well known trend of DFT methods to underestimate the band gap of crystals. Interestingly, the measured energy gap of 4.62 eV for C1–KBr pellets is closer to the DFT–GGA calculated energy gap. The weaker optical absorption structure beginning around 3.8 eV, which occurs only for the C2–KBr pellets can be associated to the existence of defects in the recrystallized cysteine samples (the existence of small monoclinic cysteine crystallites in the recrystallization powders and/or impurities is ruled out by its absence in the OC–KBr pellets). After several curve fitting trials, we have found that at least three deconvolution peaks are required to explain adequately the weaker optical absorption structure, these being assigned to the existence of defect related levels inside the band gap at 4.08 eV (A), 4.32 eV (B), and 4.57 eV (C), as shown in the inset of Figure 2.

In conclusion, the DFT calculations for the monoclinic and orthorhombic cysteine polymorphs within the GGA–PBE framework provided lattice parameters in good agreement with experimental values after geometry optimization, with lattice parameters deviations smaller than 0.04 Å. The electronic band structure results, on the other hand, suggest that both cysteine polymorphs are small gap insulators (as in the case of valine crystals [2]) due to the estimated energy gaps and the flatness of the top (bottom) valence (conduction) band curve. Thus we must conclude that the use of cysteine crystals for charge transport applications is severely

limited. Their indirect band gap also prevent their use in the development of optoelectronic devices.

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