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# ELECTRONIC STRUCTURE OF TETRAHEDRITE $Cu_{12}Tr_{0.5}Sb_4S_{13}$ (Tr = Ti, V, Fe, Ni, Cu, Zn) BY DV-Xα METHOD

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## ABSTRACT

Tetrahedrite is a non-toxic Earth-abundant mineral that has much potential as a material for thermoelectric, thin film and solar cell power generation. A recently discovered *p*-type semiconductor, it requires little processing to attain dimensionless figure of merit, *ZT*, approaching unity. Enhancements expect to see *ZT* climb above 1.0 in the near future. In this study, computer simulations using DV-Xα method were used to determine the electronic structure of $Cu_{12}Tr_{0.5}Sb_4S_{13}$ where Tr = Ti, V, Fe, Ni, Cu, Zn. It was found as the electrical conductivity increased, the band gap slightly decreased. Also, Ti and V additions make an *n*-type semimetal while iron stabilizes the tetrahedrite phase field.

KEYWORDS: *Tetrahedrite, $Cu_{12}Sb_4S_{13}$, DV-Xα, Electronic structure, ZT*

## INTRODUCTION

In the past, thermoelectric generators (TEGs) have been used only in special applications such as NASA spacecraft. Toxicity and high cost of materials are the two main factors limiting TEGs widespread use in commercial applications.

A recently re-discovered material, tetrahedrite, has changed the situation dramatically. A naturally occurring *p*-type semiconductor with a high dimensionless figure of merit, tetrahedrite is a non-toxic, abundant sulfosalt that is mined all across the Earth, primarily when silver in present in the ore.

In a 1950 study by Telkes at MIT, she found that some tetrahedrites had low resistivity of 10 μΩm and notable Seebeck coefficient of 200 μV/K [1]. After receiving little notice for over 60 years, tetrahedrite was reinvestigated by Suekuni. In 2012, he reported that stoichiometric and Ni doped tetrahedrite could attain dimensionless figure of merit, ZT, of 0.56 and 0.72 [2]. In 2013, Lu and Morelli produced a value of 0.9 ZT using raw tetrahedrite ore and doping with Zn. Furthermore, they report that high ZT values are maintained over a wide range of impurities in the ore [3]. Interestingly, they have not reported the exact values of the impurities in their ore, but have filed for a patent (WO2014008414A1). Lu and Morelli's findings are an important development because it takes us one step closer to making economically feasible non-toxic mass-produced thermoelectric devices for general use. This study is the beginning of a larger work to create an environmentally friendly TGE that can be mass produced at a low cost for the benefit of society and our planet.

The structure of tetrahedrite was proposed by Pauling and Neuman in 1934 with much controversy. Some 30 years later the structure was proven correct by Wuensch [4]. A 1983 paper by Johnson and Jeanloz showed that the stoichiometric formula is too ionically unbalanced to exist in nature. By analyzing 139 samples, they found tetrahedrite in a phase field bounded by $Cu_{12}Sb_4S_{13}$, $Cu_{14}Sb_4S_{13}$ and $Cu_{12}Sb_{4.67}S_{13}$ [5]. The necessity of a small amount of iron needed to stabilize the phase field has been argued by Tatsuka and Morimoto, else decomposition into several other phases occurs, namely famatinite and digenite with antimony coming out of solution [6]

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Tetrahedrite has space group $I\bar{4}3m$. It is formed by rotoinversion of four minimal cubic cells of $Cu_3SbS_{3.25}$. See Fig. 1. When the unit cell $Cu_{12}Sb_4S_{13}$ is doubled over, it forms a body-centered cubic (BCC) with an S(2) at the center octahedrally bonded by six Cu(2) atoms. Each of these Cu(2) atoms are bonded to two S(1) atoms in a plane referred to as 'spinners'. The Cu(2), located near the center of this triangle, is kept in check by two antimony atoms in a high amplitude-low frequency motion which disrupts the phonon transfer of heat. Combined with holes in the structure's geometry, tetrahedrite has very low thermal conductivity at 1.2 W/mK. Low thermal conductivity is desirable for good thermoelectric properties.

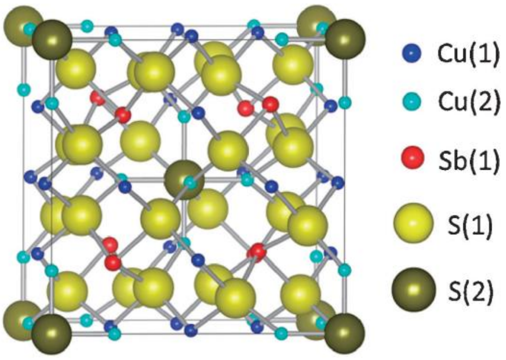

**Fig. 1.** $Cu_{24}Sb_8S_{26}$ cluster model of 95 atoms.[2]

Including only a few of the many atoms that can substitute into the formula, the original unit cell that was proposed by Pauling and Neuman is written as $(Cu, Ag)_6(Cu, Fe,Zn)_6(Sb,As)_4S_{13}$. Note that iron and/or zinc are always found in natural tetrahedrite. With as many formulas as there are authors on the subject, Wuensch's formula $^{IV}M(1)_6{}^{III}M(2)_6[^{III}X^{IV}Y_3]_4{}^{VI}Z$ is perhaps the most quoted. M(1) is predominately $Cu^+$ but also includes Fe, Zn, Ni, Ti, V, Cr, Mn, Co, Hg, Cd and Pb tetrahedrally bonded to four sulfur atoms. M(2) is Cu or Ag triangularly bonded to three sulfurs. X is Sb and As with some Bi possible bonded to three Y atoms of S with some Se or Te possible. Z is sulfur octahedrally bonded to Cu and Ag. $(Cu,Ag)_6^{TRG}[Cu_{2/3}(Fe,Zn,Cd,Hg,Pb)_{1/3}]_6^{TET}(Sb,As,Bi)_4^{SM}(S,Se)_{13}$ is the formula by Sacks and Loucks; it is helpfully descriptive.

# MATERIALS AND METHODS

## Computational Method

### *2.1 DV-Xα Method*

The discrete variational Xα method calculates molecular orbitals assuming the Hartree-Fock-Slater (HFS) approximation [11]. Starting with the molecular Hamiltonian, $\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}$ ,and invoking the Born-Oppenheimer approximation where the nuclei are in fixed positions, the nuclear kinetic energy $\hat{T}_N$ goes to zero while the nuclear potential energy $\hat{V}_{NN}$ stays constant. The resulting electronic Hamiltonian consists of an electronic kinetic energy term $\hat{T}_e$ and three potential energy terms $\hat{V}$. $\hat{H}_e$ solves the time-independent Schrödinger equation,

$$\hat{\mathrm{H}}_e \Psi_e\left(\vec{r}, \vec{R}\right) = \mathrm{E}_e\left(\vec{R}\right)\Psi_e\left(\vec{r}, \vec{R}\right) \tag{1}$$

where $\vec{r}$ is the electron position vector and $\vec{R}$ is the nuclear position vector.

In order to satisfy the Pauli exclusion principle, the Hartree-Fock wave function $\Psi^{HF}$ must follow the anti-symmetry law. This is done using a Slater determinate,

$$\left|\Psi^{HF}\left(\vec{X}_1, \vec{X}_2, \ldots \vec{X}_N\right)\right> = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1\left(\vec{X}_1\right) & \chi_2\left(\vec{X}_1\right) & \cdots & \chi_N\left(\vec{X}_1\right) \\ \chi_1\left(\vec{X}_2\right) & \chi_2\left(\vec{X}_2\right) & \cdots & \chi_N\left(\vec{X}_2\right) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_N\left(\vec{X}_2\right) & \chi_N\left(\vec{X}_2\right) & \cdots & \chi_N\left(\vec{X}_N\right) \end{vmatrix} \tag{2}$$

where $\chi_i\left(\vec{X}_i\right)$ is the $i^{th}$ orbital at the $i^{th}$ electron position and $\frac{1}{\sqrt{N!}}$ is a normalizing factor.

$$\mathrm{E}^{HF} = <\Psi^{HF}\left|\hat{\mathrm{H}}_e\right|\Psi^{HF}> = \hat{\mathrm{h}}(i) + \hat{\mathrm{J}}(i,j) - \hat{\mathrm{K}}(i,j) \tag{3}$$

where $\hat{\mathrm{h}}(i)$ is the one electron operator, $\hat{\mathrm{J}}(i,j)$ is the coulomb potential and $\hat{\mathrm{K}}(i,j)$ is the exchange term arising from the Pauli exclusion principle.
To find the ground state, minimize $\mathrm{E}^{HF}$ using Lagrange multipliers. It is found that,

$$\left[\hat{\mathrm{h}}\left(\vec{\mathrm{X}}_1\right) + \Sigma_{j\neq i}\hat{\mathrm{J}}_j\left(\vec{\mathrm{X}}_1\right) - \Sigma_{j\neq i}\hat{\mathrm{K}}_j\left(\vec{\mathrm{X}}_1\right)\right]\chi_i\left(\vec{\mathrm{X}}_1\right) = \Sigma_j \in_{ij} \chi_j\left(\vec{\mathrm{X}}_1\right) \tag{4}$$

The three operators on the left side of equation 4 are combined to form the Fock operator, $\hat{\mathrm{F}}\left(\vec{X}_1\right)$, and the orthonormal matrix $\in_{ij}$ is diagonalized. This simplifies to,

$$\hat{F}\left(\vec{X}_1\right)\chi_i\left(\vec{X}_1\right) = \in_i \chi_i\left(\vec{X}_1\right) \tag{5}$$

Equation (5) is an eigenvalue problem where $\in_i$ is the energy eigenvalue associated with orbital $\chi_i$.

Hartree-Fock method is an approximate solution to the wave equation for a many-body system in a stationary state such as a solid. Also called the self-consistent field (SCF) method, it uses Slater's Xα potential

$$V_{xc}(r) = -3\alpha\left[\frac{3}{8\pi}\rho(r)\right]^{1/3} \tag{6}$$

where $V_{xc}(r)$ is the exchange-correlation potential at position *r*, α is 0.7 - a parameter found experimentally and $\rho(r)$ is the electron density at position *r*.

The molecular electronic density is given by

$$\rho(r) = \sum_j \rho_j(r) = \sum_j f_j \left|\Psi_j(r)\right|^2 \tag{7}$$

where $f_j$ is the occupation number of the $j^{th}$ molecular orbital. The solution to the Schrödinger equation (1) is given by

$$\Psi_j(r) = \Sigma(i) C_{ij} X_i(r) \tag{8}$$

where $C_{ij}$ is a weighting coefficient and $\chi_i(r)$ is the symmetrized linear combination of atomic orbitals (LCAO) at position r.

$$\chi_i(r) = \Sigma(v,l,m) W_{vm}^{il} \phi_{nlm}^{v}(r_v) \tag{9}$$

where *v* is the atom, *l* is the orbital quantum number, *m* is the magnetic quantum number and $r_v$ is the coordinate referred to the atom *v*, which can be written as

$$\phi_{nlm}^{v}(r) = R_{nl}^{v}(r) Y_{lm}(r) \tag{10}$$

where $Y_{lm}(r)$ is taken to be the real spherical harmonics and $R_{nl}^{v}(r)$ is the radial part of the atomic orbital generated by numerical computation of the atomic problem.

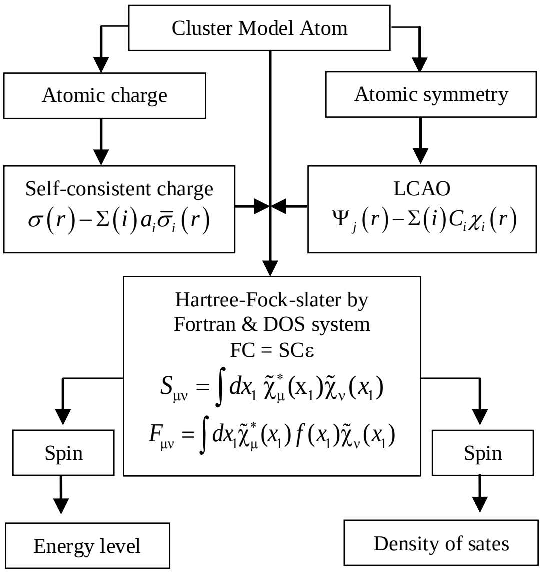

**Fig 2.** Simplified flow-chart of HFS approximation.

DV-Xα uses the Roothaan-Hall approximation,

$$\chi_i = \sum_{\mu=1}^{k} C_{\mu i} \tilde{\chi}_\mu \tag{11}$$

where $C_{\mu i}$ is a weighting factor and $\tilde{\chi}_\mu$ is an atomic orbital basis function summed over each spin orbital *i*. Substituting $\chi_i$ into the Hartree-Fock equation, multiply by $\tilde{\chi}_\mu^*(x_1)$ and integrating, we arrive at,

$$\sum_\nu C_{\nu i} \int dx_1 \tilde{\chi}_\mu^*(x_1) f(x_1) \tilde{\chi}_\nu(x_1) = \varepsilon_i \sum_\nu C_{\nu i} \int dx_1\, \tilde{\chi}_\mu^*(x_1) \tilde{\chi}_\nu(x_1) \tag{12}$$

Using the matrix element notation $F_{\mu\nu} = \int dx_1 \tilde{\chi}_\mu^*(x_1) f(x_1) \tilde{\chi}_\nu(x_1)$ and $S_{\mu\nu} = \int dx_1\, \tilde{\chi}_\mu^*(x_1) \tilde{\chi}_\nu(x_1)$ the Hartree-Fock equation can be written in matrix form as

$$\sum_\nu F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_\nu S_{\mu\nu} C_{\nu i} \tag{13}$$

Or simply as: FC = SCε (14)

Note that to avoid integrals as matrix elements, self-consistent charge (SCC) can replace SCF for bulk material.

### *2.2 Computational Details*

Classical tetrahedrite $Cu_{12}Sb_4S_{13}$ was run by DV-Xα method using the cluster model $Cu_{24}Sb_8S_{26}$ which consists of 95 atoms in a body-centered cubic (BCC) structure. The structure is as follows: 6 internal, 24 face, 24 edge copper atoms; 8 internal antimony atoms; and, 25 internal, 8 corner sulfur atoms. This cluster model has 26 td symmetry. Because this cluster was too large to run on a desktop computer, the 8 corner S(2) and 24 neighboring Cu(2) copper atoms were removed from the cluster giving us 63 atoms, all the while 26 td symmetry was maintained. This cluster ran smoothly. A band gap of 1.50 eV was calculated which is nicely between Bullett [7] and Ferreira [8] 1.2 and 1.24 eV, respectively, and Embden [9] and Johnson [5] 1.7 and 1.72 eV, respectively.

Since $Cu_{12}Sb_4S_{13}$ does not exist in nature [5] due to its lack of ionic balance, we chose to run $Cu_{12}Tr_{0.5}Sb_4S_{13}$, where Tr = Ti, V, Fe, Ni, Cu, Zn are in their 2+ ionic state. Another option would have been to run $Cu_{11}TrSb_4S_{13}$. Both of these formulas are closer to natural tetrahedrite.

The Tr atom was added to the center of the yz-plane at ±x where x=a, half the lattice parameter. This gave us a cluster model of 65 atoms with 16 S4 symmetry.

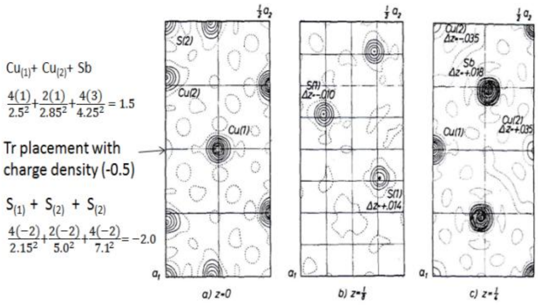

**Fig 3.** Placement of the Tr atom at (+/-x, y, z). Calculation by Coulomb’s law gives the position a charge of -0.5V. Density of state from Wuensch, 1964.

Placement of the Tr (2+) atom at the said position is justified for two reasons. First, there is a naturally occurring hole at this position with the nearest atom being sulfur at 2.234 Å – the same distance as the shortest bond length in tetrahedrite. Second, the area has an electric field of -0.5 V as shown in fig. 3.

As for our choice of Tr atoms, they were chosen for the following reasons. Fe and/or Zn are always found in natural tetrahedrite. Zn and Ni have been used as dopants by Suekuni and others. Ti and V are impurities found in the tetrahedrite in Thailand, and are thus important for future work.

Lattice parameters used in our calculation come from Wuensch, 1964. The sensitivity CVJ was set at 0.10000 for all six Tr runs. Additionally, an extra cluster model of $Cu_{12}Tr_{0.5}Sb_4S_{13}$ Tr = Cu was run at higher sensitivity CVJ 0.00100. No difference in results were detected.

## RESULTS AND DISCUSSION

Computations of energy level, density of states and internal energy were obtained for the six transition metals. It was seen that as Tr increased in atomic number and the 3d orbital filled up and therefore electrical conductivity increased, the band gap decreased slightly. See fig. 4.

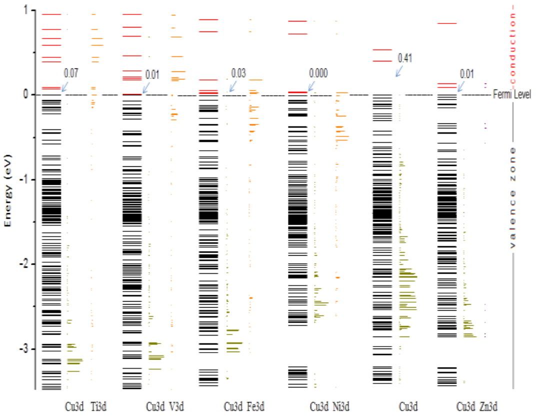

**Fig 4.** Band gaps with Cu 3d and Tr 3d electron shells where Tr = Ti, V, Fe, Ni, Cu, Zn

As can be seen, the transition metals are potentially tunable and only the right combination of elements are needed to improve performance.

Seebeck coefficients for $Cu_{12}Tr_{0.5}Sb_4S_{13}$ were calculated by,

$$S=\frac{\pi^2 k_B^2 T}{3eE_F}\left(\frac{3}{2}+r\right) \qquad (15)$$

Where $k_B$ is Boltzmann’s constant, $e$ is absolute value of the charge carrier, $T$ is absolute temperature, $E_F$ is energy at the Fermi level, and r is the number of molecular orbitals.

**Table 1.** $E_F$ and Seebeck coefficient for $Cu_{12}Tr_{0.5}Sb_4S_{13}$. $E_F$ obtained from dd7 file.

| Tr | Ti | V | Fe | Ni | Cu | Zn |
|---|---|---|---|---|---|---|
| $E_F$ | 0.64 | 0.17 | -0.21 | -0.52 | -2.26 | -2.64 |
| S | 155 | 584 | 496 | 191 | 34 | 38 |

For positive Fermi energies, $E_F$, Table 1 shows that Ti and V additions to tetrahedrite create n-type thermoelectric materials. This is the first known reporting of an *n*-type tetrahedrite thermoelectric material.

The goal is a high dimensionless figure of merit, ZT.

$$ZT = \frac{\sigma S^2 T}{\kappa} \qquad (16)$$

where $\sigma$ is electrical conductivity, $S$ is Seebeck coefficient, $T$ is absolute temperature, and $\kappa$ is thermal conductivity. Due to the interdependence of $\sigma$, $S$ and $\kappa$, ZT must take into account all factors. For instance, filling of the 3d electron shell increases σ, but also increases $\kappa$. Most researchers have focused on reducing the thermal conductivity while attempting to keep electrical conductivity and Seebeck coefficient high.

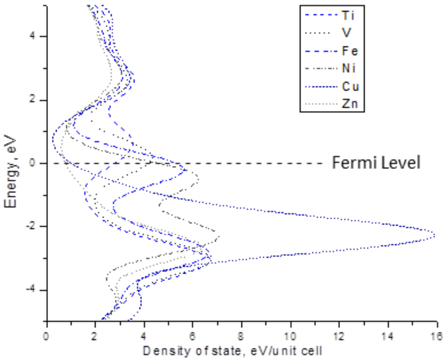

**Fig 5.** Total density of states for the six substituted Tr atoms.

The peaks of Cu, Zn and Ni in fig. 5 give these three elements good potential for increasing ZT. Meanwhile, Fe, Ti and V are spread across the Fermi level making them less ideal. But these 3d orbitals are tunable so it is hoped that the tetrahedrite in Thailand has more zinc content than iron allowing more flexibility in improving ZT in future experimental trials.

In table 2, bond energies show that iron stabilizes the tetrahedrite phase field. The stabilizing effect is due to iron’s ability to switch between ionic 2+ high spin ($3d^6$) states and 3+ low spin ($3d^5$) states. For S(2)-Cu(2) bonds with iron present, the result was three bonds at 0.92 units, while the same bond with other transition metals resulted in three different energies. With Fe, Cu(2)-S(1) had six stable bonds at 1.62 to 1.83, yet the other elements showed 16 weaker bonds in an unstable scattering of energy. Therefore, it is noted that iron has a stabilizing effect on all six bonds when added to the structure. This result is supported by Tatsuka where he found that tetrahedrite without iron decomposes into famatinite, digenite, and antimony [6].

**Table 2.** Atomic bond, bond length, and associated bond energies for Tr = Fe and the other five substitute elements with Ni used for the average. Ti, V, Cu and Zn results were nearly identical to Ni.

| Bond | Å | Fe | Ti, V, Ni, Cu, Zn |
|---|---|---|---|
| S2-Cu2 | 2.23 | (3)0.92 | 0.64, 0.82, 1.19 |
| S2-Cu1 | 2.27 | 1.85, 2.02, 2.03 | (4) 0.5, 1.0, (2) 1.5 |
| Cu2-S1 | 2.34 | (2) 1.62, (4) 1.8 | (16) 0.39 -1.38,0.67 |
| S1-Sb | 2.45 | 1.53, (2) 1.86 | (6) 0.45, 1.18, (6)1.37 |
| S1-Tr | 2.23 | 1.81 | 0.39, 1.32 |
| Cu1-Tr | 2.51 | (2) 0.9 | (3) 0.17, 0.46, 0.64 |

Furthermore, results of an MXDOTRO simulation of tetrahedrite by Rittiruam [12] are in agreement with Tatsuka. It is predicted that a future MXDORTO simulation of tetrahedrite with a small addition of iron will show a tetrahedrite with a thermodymanically more stable structure compared to tetrahedrite without iron.

## CONCLUSION

It was found that as the electrical conductivity increased, the band gap slightly decreased. Ti and V in tetrahedrite can make *n*-type semimetals while Fe, Ni and Zn make *p*-type. Furthermore, the transition metals should be tunable for higher ZT values while iron stabilizes the tetrahedrite phase field.

## ACKNOWLEDGEMENTS

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