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Study of Thermoelectric Properties of $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe) Systems using Spin-Polarized Density Functional Theory

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***Abstract**: We have investigated the thermoelectric properties of the $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe; x = 0, 0.25, 0.50, 0.75) systems, by combining the electronic structures achieved from first principles calculations with the semi-classical Boltzmann transport theory. The calculated band structures and density of states plots evidently show the half-metallic ferromagnetic behavior for the $Zn_{1-x}TM_xS$ (TM=Cr/Fe) systems and ferromagnetic semiconducting character for $Zn_{1-x}Mn_xS$ systems. The transport coefficients such as Seebeck coefficient, electrical conductivity, thermal conductivity, power factor and figure of merit are calculated. The two-current model is employed to calculate the total Seebeck coefficient. The calculated transport co-efficients convey that $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe) systems can be utilized as potential thermoelectric materials.*
***Keywords**: Thermoelectric properties, ZnS, Transition metal, BoltzTraP, DFT*

I. INTRODUCTION

The increasing energy crisis demand for efficient thermoelectric (TE) materials, which can convert waste heat into useful electrical energy. To encounter this issue, scientific society look forward to potential thermoelectric materials, which can perform at high temperatures. The efficiency of a TE material is evaluated by dimensionless figure of merit (*ZT*). The *ZT* is defined as $ZT = S^2\sigma T/(\kappa_e+\kappa_L)$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κ_e and κ_L are the electrical and lattice contribution to the total thermal conductivity κ, respectively [1]. An effective thermoelectric material should have high Seebeck coefficient, high electrical conductivity and low thermal conductivity. Parameters in the figure of merit are greatly dependent on each other, which need optimization to achieve high *ZT*. Numerous studies were performed, both experimentally and theoretically to recognize novel thermoelectric materials and to improve the *ZT* of the existing TE materials and it is evident that one can improve the efficiency of TE materials by doping, nano-structuring and alloying etc., [2, 3].

One of the most important II-VI semiconductor compounds, Zinc sulfide (ZnS) with a direct band gap of 3.82 eV [4] in the zinc-blende (ZB) structure has attracted much attention due to its promising applications such as light emitting diodes (LED), dye-sensitized solar cells, nano-sensors, and photo catalysts. Its lattice constant and other band parameters can be easily tuned by varying the ionic composition [5]. In the present study, we are attempting to explore innovative materials for thermoelectric applications through investigations on thermoelectric properties of $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe; x = 0, 0.25, 0.50, 0.75) systems by combining the electronic structures calculated from first principles calculations with the second-principles method: BoltzTraP code [6]. We have chosen these systems with the expectation that they would exhibit half metallicity and good thermoelectric properties.

II. COMPUTATIONAL DETAILS

The present calculations are performed using the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method based on Density Functional Theory (DFT) [7] as implemented in the WIEN2K program developed by Blaha and co-workers [8]. The exchange correlation effect is treated by using modified Becke-Johnson Local Density Approximation (mBJLDA) [9], [10]. In this method the basis set is achieved by dividing the cell into non-overlapping muffin-tin (MT) spheres centered at the atomic sites and an interstitial region (IR). The potential and the charge density are expanded in terms of spherical harmonics inside the MT sphere and by plane wave basis set in the IR region. To achieve the energy convergence of the eigenvalues, we use a k cut-off, $k_{max}=7.0/R_{MT}$, where R_{MT} is the smallest atomic sphere radius (muffin-tin radius) and k_{max} denotes the magnitude of the largest k-vector in the plane wave expansion. The valence wave functions are augmented up to l_{max}= 10 inside the muffin-tin sphere, while the charge density is Fourier expanded up to G_{max}= 12 $(Ry)^{1/2}$. The R_{MT} of Zn, S and TM (TM=Cr/Mn/Fe) atoms are set to 2.02, 1.76 and 2.02 a.u., respectively. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-4} Ry.

The transport properties such as Seebeck coefficient, electrical conductivity, electronic thermal conductivity, power factor and figure of merit of $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe; x = 0, 0.25, 0.50, 0.75) systems are calculated using the BoltzTraP code that involves the semiclassical Boltzmann transport equation under the constant relaxation time (τ) approximation. A dense mesh of 10,000 k points in the first Brillouin zone is employed for calculating thermoelectric properties of $Zn_{1-x}TM_xS$. In the constant relaxation time approximation, the electrical conductivity, electronic thermal conductivity and power factor can be calculated in terms of τ whereas Seebeck coefficient and electronic figure of merit are independent of τ.

III. RESULTS AND DISCUSSION

A. Structural and Electronic Properties

The structural properties of ZnS and $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe) compounds are calculated using Perdew-Burke-Ernzerhof–Generalized Gradient Approximation (PBE–GGA). The space group of binary ZnS is *F-43m* (No. 216) and the atomic positions of Zn and S atoms are selected at (0, 0, 0) and (1/4, 1/4, 1/4), respectively. To design $Zn_{1-x}TM_xS$ systems, eight atoms supercell is constructed and the Zn atom (1, 2, 3 for x = 0.25, 0.50, 0.75, respectively) is substituted by transition metal (TM=Cr/Mn/Fe) atom. Ultimately, new compounds retain cubic symmetry with the space group *P-43m* (No. 215) when x = 0.25 and 0.75, while for x = 0.50 alone they attain tetragonal symmetry with the space group *P-4m2* (No. 115). From our resultant spin-polarized electronic band structures and density of states of the $Zn_{1-x}TM_xS$ system, the spin-polarized thermoelectric properties are calculated by employing the semi-classical Boltzmann theory as incorporated within BoltzTraP code.

B. Thermoelectric Properties

Thermoelectric properties of the investigated compounds are calculated for temperature range between 100 K and 1000 K. The calculated Seebeck coefficient (S), electrical conductivity (σ/τ), electronic thermal conductivity (κ_e/τ), power factor ($S^2\sigma/\tau$) and electronic figure of merit (ZT_e) for $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe: x = 0, 0.25, 0.50, 0.75) systems are shown in Fig. 1-3. The above quantities are first calculated for both the spin channels and then the total S is calculated by two current model [11, 12] using the following expression,

$$S = \frac{S_{\uparrow}(\sigma_{\uparrow}/\tau_{\uparrow}) + S_{\downarrow}(\sigma_{\downarrow}/\tau_{\downarrow})}{(\sigma_{\uparrow}/\tau_{\uparrow}) + (\sigma_{\downarrow}/\tau_{\downarrow})} \quad (1)$$

and the total σ/τ and κ_e/τ are calculated by adding their spin up and spin down contributions with the assumption that $\tau_{\uparrow} = \tau_{\downarrow}$. For matching the calculated thermoelectric properties with the experimental results, one has to consider the temperature dependence of relaxation time and that $\tau_{\uparrow}(T) \neq \tau_{\downarrow}(T)$ [13, 14].

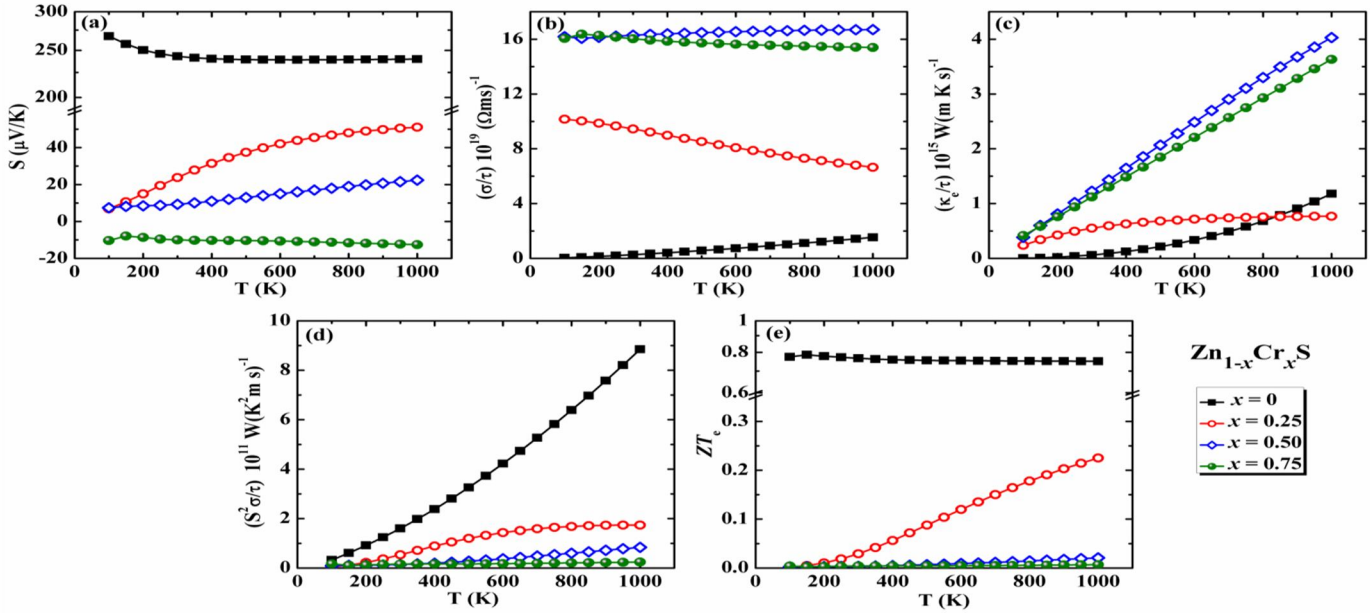

Fig. 1: Variation of transport coefficients with temperature, (a) Seebeck co-efficient, (b) electrical conductivity, (c) thermal conductivity, (d) power factor and figure of merit for $Zn_{1-x}Cr_xS$ (x = 0, 0.25, 0.5, 0.75) systems.

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The calculated Seebeck coefficient (S) for the semiconducting ZnS system is ~267 μV/K at 100 K [Fig. 1(a)]. It decreases up to room temperature (RT) and remains almost constant (~240 μV/K) in the temperature range RT-1000 K. When the Cr atoms substitute Zn atoms, then ZnS changes from semiconducting nature to half metallic ferromagnets as understood from our band structure and density of states results and the magnitude of S value increases with the increasing temperature. However, this value decreases for the increase of Cr concentration (x) at each temperature since S is proportional to $m^*T/n^{3/2}$ for metallic and degenerate semiconductors and the metallic nature or n value increases with Cr concentration. Here, m^* and n are effective mass of charge carriers and carrier concentration, respectively. The modulus of S is obtained as ~24 μV/K for x = 0.25 case and ~ 10 μV/K for both x = 0.5 and 0.75 cases at RT and 51 μV/K, 22 μV/K and 13 μV/K for x = 0.25, 0.5 and 0.75, respectively at 1000 K.

The electrical conductivity per unit relaxation time (σ/τ) increases gradually with temperature for ZnS [Fig. 1(b)]. This can be owed to the increase in carrier density n with temperature in this semiconductor according to the expression $\sigma/\tau = ne^2/m^*$. Though $\sigma(T)$ is more dominated by $n(T)$ than $\tau(T)$ in the case of semiconducting system, it is mainly determined by $\tau(T)$ in the case of metals in which temperature dependence of n is less considerable. Due to this reason, for the Cr substituted half metallic $Zn_{1-x}Cr_xS$ systems, the nature of σ/τ curve in Fig. 1(b) can be associated only with the least temperature dependence of n. It is well known fact that the σ value has to be found instead of σ/τ for the comparison with experimental results. In fact, the relaxation time decreases with the increase of temperature because of electron scattering and, moreover, the calculation of temperature dependence of τ is more complicated process. For metals and semiconductors, the temperature dependent relaxation time is in a typical range of 10^{-14} to 10^{-15} s [15]. With the increasing Cr concentration, the carrier density n also increases and hence the value of σ/τ also increases at a particular temperature. Still, Fig. 1(b) infers that the value of σ/τ for x = 0.5 (tetragonal symmetry) is almost close to or a little higher than that for x = 0.75 (cubic symmetry) which could be due to lesser m^* in the former compared to that in the latter. Fig. 1(c) shows the temperature dependence of electronic thermal conductivity following the Wiedmann-Franz law ($\kappa_e = L\sigma T$, $L = 2.45\times10^{-8}$ $W\Omega K^{-2}$ is Lorentz constant).

Power factor ($S^2\sigma/\tau$) and electronic figure of merit (ZT_e) as a function of temperature [Fig. 1(d-e)] are used to optimize the temperature range at which substantial thermoelectric properties can be gained. Since ZT_e becomes equal to S^2/L, this electronic figure of merit is merely depending on S. For ZnS, ZT_e is ~0.77 at RT and remains almost the same in the temperature range RT-1000 K. With the increasing Cr concentration, it decreases to ~0.291, 0.003 and 0.004 for x = 0.25, 0.5 and 0.75 cases, respectively, at RT. There is a moderate increase with temperature and reaches to the value of ~0.225, 0.021 and 0.007 for these three concentrations, respectively. In fact, these calculated ZT_e values are overestimated comparing with the actual thermoelectric figure of merit ZT which consists of lattice part of thermal conductivity κ_L (which might be higher than the electronic part in magnitude at low temperatures) also. All these thermoelectric parameters are showing a gradual change with x (from 0 to 0.25 to 0.75) at a particular temperature due to their similar cubic symmetry. However, $Zn_{0.50}Cr_{0.50}S$ attains tetragonal symmetry and show similar behaviour to that of $Zn_{0.25}Cr_{0.75}S$.

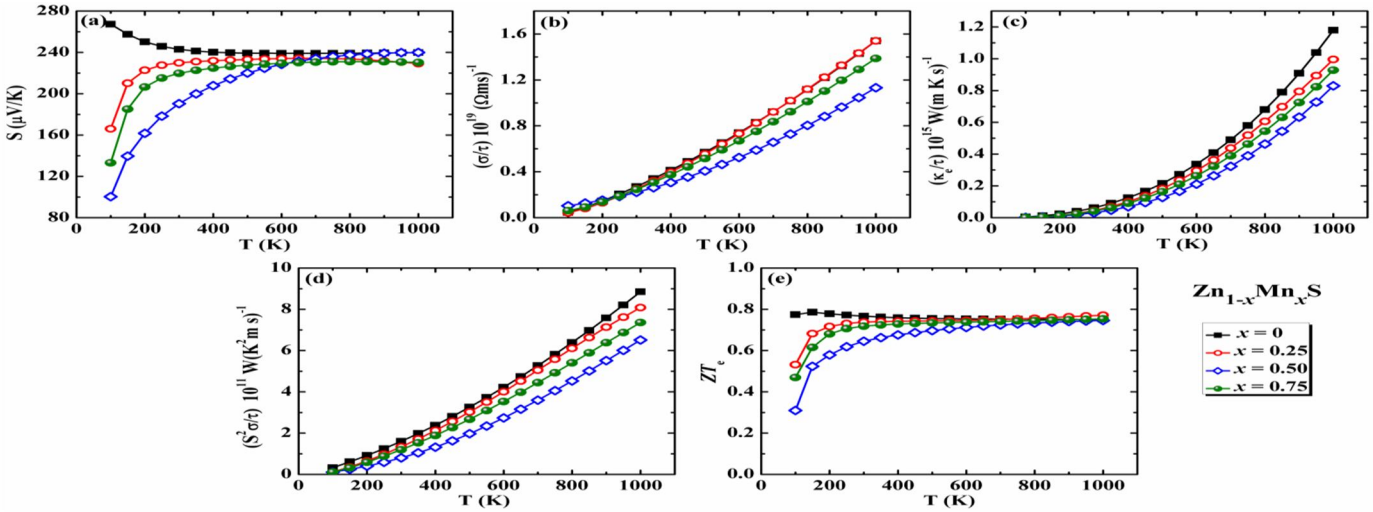

Fig. 2: Variation of transport coefficients with temperature, (a) Seebeck co-efficient, (b) electrical conductivity, (c) thermal conductivity, (d) power factor
and figure of merit for $Zn_{1-x}Mn_xS$ (x = 0, 0.25, 0.5, 0.75) systems.

The $Zn_{1-x}Mn_xS$ (x = 0.25, 0.5 and 0.75) systems exhibit semiconducting behavior. The calculated temperature dependent parameters S, σ/τ, κ_e/τ, $S^2\sigma/\tau$ and ZT_e for all the $Zn_{1-x}Mn_xS$ (x = 0.25, 0.5 and 0.75) systems exhibit almost similar behaviour like the host except at low temperature range where a gradual increase occur in both S and ZT_e with the increasing temperature [Fig. 2(a) and 2(e)]. We observed that the tetragonal symmetry differentiates the thermoelectric properties of $Zn_{0.50}Mn_{0.50}S$ system from the other cubic systems. At RT, the S value is 243 μV/K, 230 μV/K, 190 μV/K and 220 μV/K and the ZT_e value is 0.77, 0.74, 0.65 and 0.72 for $Zn_{1-x}Mn_xS$ (x = 0, 0.25, 0.5 and 0.75), respectively.

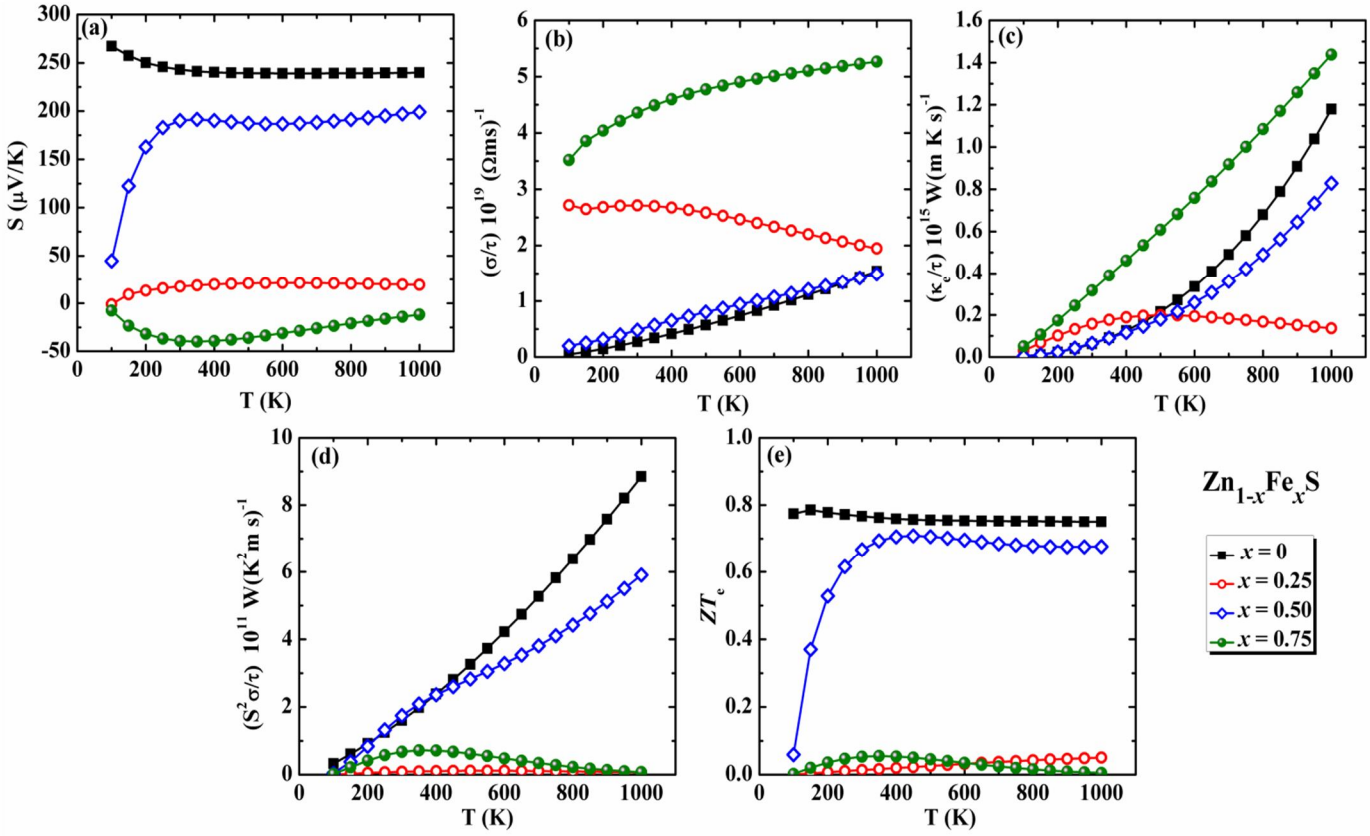

Fig. 3: Variation of transport coefficients with temperature, (a) Seebeck co-efficient, (b) electrical conductivity, (c) thermal conductivity, (d) power factor and figure of merit for $Zn_{1-x}Fe_xS$ (x = 0, 0.25, 0.5, 0.75) systems.

In the case of Fe substitution, the thermoelectric characteristics for cubic $Zn_{0.75}Fe_{0.25}S$ and $Zn_{0.25}Fe_{0.75}S$ systems [Fig. 3(a-e)] have close resemblance to $Zn_{0.75}Cr_{0.25}S$ and $Zn_{0.25}Cr_{0.75}S$ systems, respectively [Fig. 1(a-e)] but, in the case of $Zn_{0.50}Fe_{0.50}S$ with tetragonal symmetry, they look like those of $Zn_{0.50}Mn_{0.50}S$ [Fig. 2(a-e)] because of its nearly semiconducting behaviour. The main thermoelectric parameters S and ZT_e at RT are given as ~18 μV/K, 190 μV/K and 39 μV/K and 0.013, 0.667 and 0.053 for for $Zn_{1-x}Fe_xS$ (x = 0.25, 0.5, 0.75), respectively.

IV. CONCLUSIONS

A systematic investigation of thermoelectric properties $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe: x = 0, 0.25, 0.5, 0.75) systems is performed by combining the electronic structures obtained from first principles calculations with Boltzmann transport theory. The transport coefficients of the $Zn_{1-x}TM_xS$ systems as a function of temperature are calculated. All the investigated systems exhibit thermoelectric behaviour. The calculated transport co-efficients reports that $Zn_{1-x}TM_xS$ (TM=Cr/Mn/Fe) systems can be employed as possible thermoelectric materials. Since $Zn_{1-x}Mn_xS$ (x = 0, 0.25, 0.5 and 0.75) systems exhibit semiconducting character and $Zn_{0.50}Fe_{0.50}S$ shows nearly semiconducting nature with considerable thermoelectric properties, one can synthesize them with less lattice thermal conductivity by grain size reduction or nanostructures formation and utilize them as potential candidates for efficient power generation.

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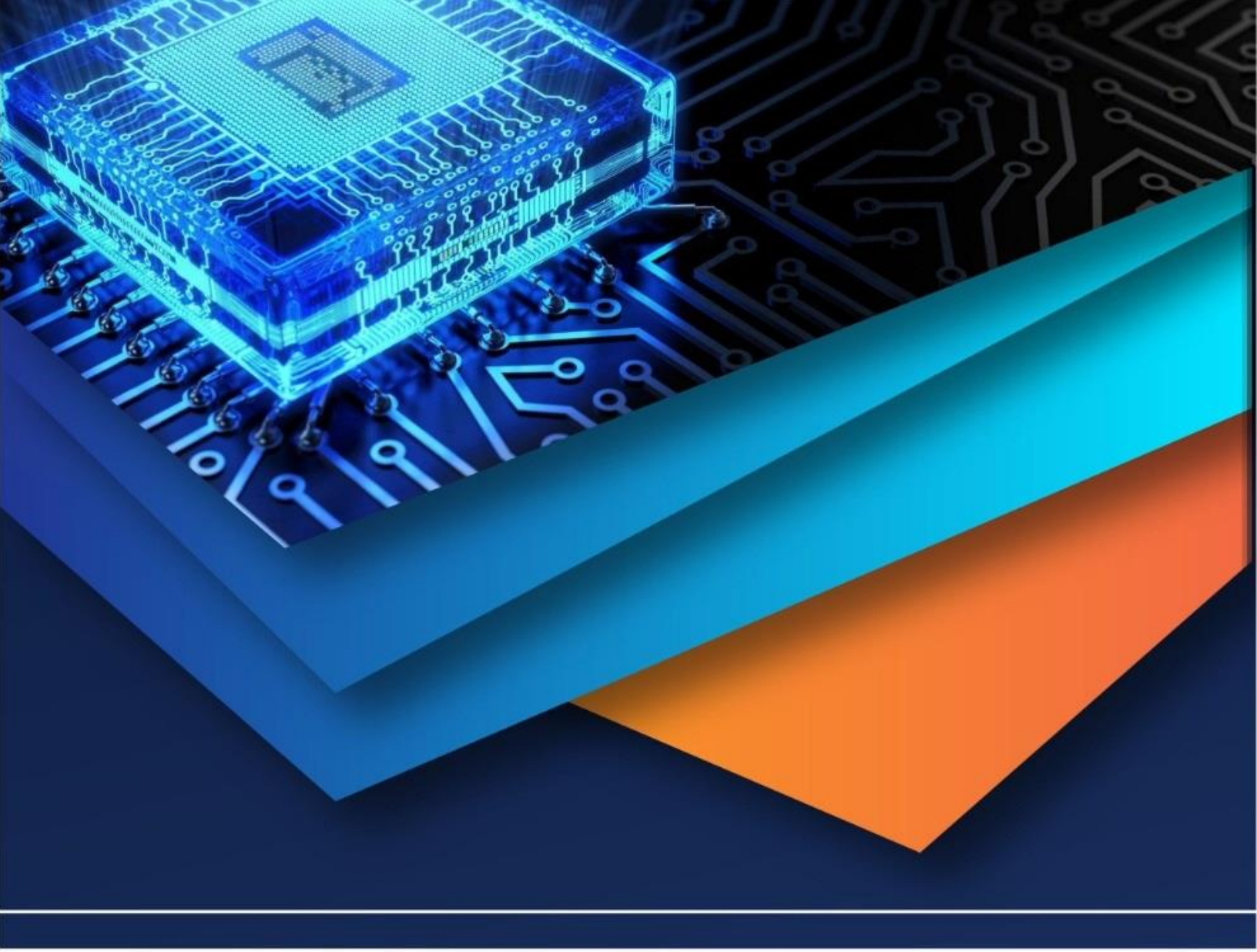

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