Electronic structure, magnetism and lattice dynamics of new ThXAsN (X=Fe,Co,Ni) superconductors: A First Principles Study

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In this work, we present a comparative study of mechanical properties, electronic structure, magnetism and lattice dynamics of three different systems namely ThFeAsN, ThCoAsN and ThNiAsN which possess same crystal structure. Experimentally it is well established that ThFeAsN and ThNiAsN show superconducting properties. However, ThCoAsN compound is not experimentally synthesized. We evaluate the elastic constants of all these systems and it turns out that, these systems are mechanically stable. We found substantial differences in the electronic structures of these three compounds in terms of density of states, band structures and Fermi surfaces. We also present the band structure of ThFeAsN in the anti-ferromagnetic ground state which appears to be the theoretical ground state of the system. Role of spin-orbit coupling in the electronic structures of these three systems is also discussed. For ThFeAsN system, spin-orbit coupling primarily influence the hole pockets around Γ point, where the largest superconducting gaps are usually found. Low energy electronic structures of the other two systems are hardly affected by spin-orbit coupling. Our phonon calculation reveals that all the systems including the ThCoAsN system are dynamically stable. Phonon dispersion relations indicate that optical modes of all the three systems are almost the same but there are significant variations in the lower frequency manifold consisting of mixed modes. We also evaluate the electron-phonon coupling constants as well as superconducting transition temperatures for all three systems within Eliashberg formalism. Our electron-phonon calculation predicts a $T_c$ of 5.4 K for the ThCoAsN system. But the evaluated electron-phonon coupling constant for ThFeAsN, give rise to a $T_c < 1$ K as compared to the experimental $T_c$ of 30 K. However, the value of $T_c$ is increased considerably (~15 K) when we take into account the amplifying effects of anti-ferromagnetic spin density wave order and out of plane soft phonon modes.

I. INTRODUCTION

Since the discovery of high temperature superconductivity in LaFeAs(O, F)\textsuperscript{11}, a large number of new Fe-based superconductors (SCs), popularly known as pnictides, have been found. Most of those Fe-based SCs are generally categorized into six families depending upon their chemical compositions, namely 11, 111, 112, 122, 1111 and 42622 (some times denoted as 21311)\textsuperscript{2}. Apart from that, two newly discovered families 112 and 1144 also show some unique features which are not usual characteristics of Fe-based SCs\textsuperscript{3,4}. All these systems have tetragonal crystal structure with FeAs/FeSe layer as the basic building block which seems to play an important role in superconductivity. Along with these Fe-based SCs, some Ni/Co based iso-structural systems with or without superconducting properties have also been reported\textsuperscript{5,6}. For example, 1111 type nickel based pnictides like LaNiAsO were reported with superconducting transition temperature of 2.75 K\textsuperscript{5}. On the other hand, LaCoAsO is an itinerant ferromagnet\textsuperscript{5} with no trace of superconductivity. Similarly BaCo$_2$As$_2$ which is iso-structural to another Fe-based superconductor BaFe$_2$As$_2$ is also reported with no superconductivity\textsuperscript{10}. Apart from its novel unconventional superconducting property, Fe based SCs display a number of exotic normal state properties such as spin density wave (SDW), orbital density wave (ODW), structural transition, nematic order etc., which are very different from all other classes of high temperature SCs including high $T_c$ cuprates\textsuperscript{11–15}. Although nickel-based pnictides posses the same crystal structure as that of the Fe-pnictides, the superconducting pairing mechanism in these systems are different from that of the Fe-based SCs. In general, superconducting $T_c$ of nickel-based pnictides can be estimated fairly accurately by Eliashberg formalism of electron-phonon coupling mediated superconductivity\textsuperscript{16,17}. Recent studies show that, the role of electron-phonon coupling in Fe-based SCs has been understated specially in the presence of anti-ferromagnetic type spin density wave ground state\textsuperscript{18–20}. Fe pnictides as well as Ni pnictides both have layered structure with (Fe/Ni)As layer as the main building block, height of this As/Se atom from the Fe/Ni plane defines ‘anion height’, which is closely related to $z_{\text{As}}$ i.e., the fractional co-ordinate of As atom, plays a major role in most of the exotic phases discussed above for Fe-based SCs\textsuperscript{21,22}. However, the role of anion height in the Ni/Co based iso-structural system is not well studied as it has no major role in influencing the low energy electronic structure. Being multi-orbital nature, Fermi surface topology of Fe-based SCs is also very different from other high $T_c$ SCs and is very sensitive to temperature, pressure and impurity/doping. Sign changing $s^\pm$ superconducting order parameter is widely accepted by the scientific community for describing various physical properties of Fe-based SCs but there are conclusive
evidences of deviation of $s^\pm$ pairing scenario. Therefore, pairing symmetry of these SCs is still under considerable debate [23–27]. In general, Fe-based SCs have high critical current density as well as high upper critical magnetic field ($H_{c2}$). Added to that it posses moderate anisotropy (important for transport of charge) and ductility which give these SCs edge over high $T_c$ cuprates as far as superconducting applications are concerned [28]. These Fe-based SCs have all the potential to be the next generation SCs. Therefore, a better theoretical understanding of these system will accelerate the development of more sophisticated technologies based on pnictides SCs.

Superconductivity in the stoichiometric ThFeAsN compound in ambient pressure with remarkably high $T_c$ of 30K was recently reported [29]. This new 1111-type FeAs-based compound with a ZrCuSiAs-type structure, where the (LaO) layers in LaOFeAs are replaced by a ThN layer. Unlike ReFeAsO series, this newly discovered Fe-based SC does not show any long range magnetic order. However, evidence of strong magnetic fluctuations above 35 K was found via muon spin rotation/relaxation and nuclear magnetic resonance techniques [30]. Th(Fe/Ni)AsN have distinctively shorter c-axes (a-axes are similar) as compared to the La(Fe/Ni)AsO series of Fe/Ni-based SC. This suggests that these three systems posses an in built uni-axial nature superconductivity in ThFeAsN, without intrinsic doping (or external pressure) and the absence of long range magnetic order, probably indicate a consequential deviation from the standard $s^\pm$ pairing scenario with respect to previous FeAs-based SCs. Thus the study of low energy electronic structures will provide a wealth of information. Recent work of Johnson et al., shows that, spin-orbit effect lifts the degeneracy of Fe $d_{yz}$ and $d_{xz}$ orbital at $\Gamma$ point which leads to orbital ordering in FeTe(Se) systems [31]. Therefore, study of electronic structure in the presence of spin-orbit coupling will provide important insights about superconductivity in ThFeAsN. Moreover, recent discovery of room temperature superconductivity in a number of compounds including solidified H$_2$S (under hydrostatic pressure) and its close proximity to electron phonon couplings, challenge the general consensus of high temperature superconductivity [32–35]. It is also established that superconductivity in structurally similar compound ThNiAsN is phonon mediated and superconducting transition temperature estimated from density functional perturbation theory within Eliashberg formalism is around 3.5K which is consistent with the experimentally measured $T_c$ of 4.3K [34, 35]. Therefore, it is important to study the role of electron-phonon coupling in superconductivity of ThFeAsN compound. First principles investigation on ThFeAsN system reveals an stripe antiferromagnetic ground states on contrary to the experimental ground state with no long range magnetic order [36, 37]. Current studies which include the role of AFM/SDW order on electron phonon coupling for various Fe-based SCs (like FeSe, LiFeAs etc.) explain the experimental $T_c$ of these systems as well as the pressure dependence of $T_c$ [38]. From these works, it is established that, one should consider the combined effect of AFM order and soft out of plane lattice vibration on electron phonon coupling to predict the experimentally observed $T_c$. Electronic structure calculations disclose that ThFeAsN is a semi-metal and posses a partially nested electron and hole like Fermi pockets [39]. On the other hand, ThNiAsN posses a quite different electronic structure from that of the ThFeAsN with no magnetic ordering as evident from latest theoretical studies [35]. We also consider a structurally similar compound ThCoAsN and predicts its mechanical properties, electronic structures and lattice dynamical properties. A comparative study of ThXAsN (X=Fe,Co,Ni) will elucidate mechanism of superconductivity in these compounds and this is the main goal of this paper.

In this work, first, we calculate the values of elastic constants and elastic moduli of ThXAsN (X=Fe,Co,Ni) and show that these systems are mechanically stable. We also point out some of the important mechanical properties of these systems from the application point of view. Apart from the mechanical properties we also evaluate the plasma frequencies of the system along different axes to predict the effective dimensionality of these systems and then compare these values with various others Fe-based SCs. Next, we discuss the magnetic ground states of all these systems. We present our calculated electronic structures of ThXAsN (X=Fe,Co,Ni) for non-magnetic as well as stabilized magnetic ground states (AFM for ThFeAsN and FM for ThCoAsN). A systematic study of DOS, band structure and FS have been performed. Effect of spin-orbit coupling in the electronic structure of these three systems is also discussed. Finally, we present our phonon dispersion relations for ThXAsN (X=Fe,Co,Ni). We also evaluate superconducting transition temperature within Eliashberg theory. Role of electron-phonon coupling in superconducting properties of these systems is also analysed. In case of ThFeAsN, we also discuss the possible amplification of electron-phonon coupling constant in the presence of AFM ground state.

II. CRYSTAL STRUCTURE AND COMPUTATIONAL METHODS

The crystal structures of ThXAsN (X=Fe,Co,Ni) are tetragonal with space group symmetry $P4/nmm$ (space group no. 129) with two formula per unit cell as shown in Fig.1. Experimental lattice parameters of ThFeAsN ($a = 4.0414\,\text{Å}, c = 8.5152\,\text{Å}$), ThNiAsN ($a = 4.0804\,\text{Å}, c = 7.9888\,\text{Å}$) are used as the input of our first principles density functional theory calculations [23, 34]. All atomic positions were relaxed. Since ThCoAsN system has not been prepared experimentally, we take the experimental lattice parameters as well as atomic positions.
of both ThFeAsN and ThNiAsN systems as the initial guess for the ThCoAsN system. Then we perform full geometry optimization to get the lattice parameters and atomic positions of ThCoAsN. Our predicted lattice parameters for tetragonal non-magnetic ThCoAsN system is $a = 4.057\,\text{Å}$, $c = 8.351\,\text{Å}$, and $z_{\text{As}} = 0.6404$ (fractional $z$ co-ordinate of As atom), $z_{\text{Th}} = 0.1377$ (fractional $z$ co-ordinate of Th atom). In TABLE I, we present our relaxed atomic position as well as experimental lattice parameters of ThFeAsN and ThNiAsN systems. Apart from that we also depict the fully optimized structural parameters of ThCoAsN system in TABLE I. It is a well established fact that for Fe-based SCs, density functional theory within GGA underestimate the relaxed atomic position of As atom ($z$ co-ordinate of As atom) or particularly the anion height. The reason of this underestimation is the strong magnetic fluctuation associated with the Fe atom. In case of ThFeAsN, strong magnetic fluctuations above 35 K were already reported [30]. We observe a change of 2.03% in the fractional $z$ co-ordinate of As atom as a result of atomic position relaxation with respect to the experimental value. Moreover, electronic band structure calculated using fully experimental structural parameters is different from that of the calculated using atomic position relaxed crystal. In the appendix, we discuss the differences in the electronic structure for these two cases. Our first principles geometry optimization is performed by employing the projector augmented-wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [41,42]. Exchange-correlation functional has been treated under generalized-gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [43].

All internal atomic positions are relaxed with an energy convergence of $10^{-8}$ eV. The sampling of the Brillouin zone was done using a $\Gamma$-centered $10 \times 10 \times 5$ Monkhorst-Pack grid. Forces are minimized to less than 0.0001 eV/Å in the relaxation. For the Fermi surface calculations a denser k-grid of size $20 \times 20 \times 20$ is chosen.

FIG. 1: Crystal structure of ThFeAsN (ThNiAsN and ThCoAsN possess same crystal structures)

TABLE I: Theoretical atomic positions and experimental lattice parameters of ThFeAsN and ThNiAsN systems. Theoretical lattice parameters and atomic positions of ThCoAsN within GGA.

|          | GGA  | $a$    | $c$     | $z_{\text{As}}$ | $z_{\text{Th}}$ |
|----------|------|--------|---------|-----------------|-----------------|
| ThFeAsN  | 4.0414 | 8.5152 | 0.6388  | 0.1382          |                 |
| ThNiAsN  | 4.0804 | 7.9888 | 0.6405  | 0.1396          |                 |
| ThCoAsN  | 4.0570 | 8.3519 | 0.6404  | 0.1377          |                 |

The elastic constants of ThFeAsN are determined by using the linear-response stress-strain method, as implemented in the VASP code [44]. Under a small strain ($\epsilon_{kl}$), the corresponding stress ($\sigma_{ij}$) within Hook's law can be written as $\sigma_{ij} = C_{ijkl}\epsilon_{kl}$, where $C_{ijkl}$ is the stiffness tensor which consist of elastic constants of the crystal. Depending on the crystal symmetry, the total number of elastic constants can be varied. For example, a cubic lattice has only three elastic constants of $C_{11}$, $C_{12}$ and $C_{44}$. On the other hand, a tetragonal lattice structure like the present system (ThFeAsN) has six independent elastic constants namely $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$ and $C_{66}$. Bulk moduli (B) and shear moduli (G) in Voigt (V) and Reuss (R) approximations is given by [45–47],

- $B_{v} = 1/9\{2(C_{11} + C_{12}) + C_{33} + 4C_{13}\};$
- $G_{v} = 1/30\{M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}\};$
- $B_{R} = C^{2}/M;$
- $G_{R} = 15\{18B_{v}/C^{2} + 6/(C_{11} - C_{12}) + 6/C_{44} + 3/C_{66}\}^{-1};$

where, $C^{2} = C_{33}(C_{11} + C_{12}) - 2C_{13}^{2}$
and $M = C_{11} + C_{12} + 2C_{33} - 4C_{13}$.

Under Voigt-Reuss-Hill (VRH) approximation [45–47],

- $B_{H} = (B_{v} + B_{R})/2;$
- $G_{H} = (G_{v} + G_{R})/2.$

The Youngs modulus $Y$ and the Poissons ratio ($\nu$) can be written in terms of B and G as

- $Y = 9BG/(3B + G);$
- $\nu = (3B - 2G)/(2(3B + G)).$
All the phonon calculations are performed using Quantum ESPRESSO package, which utilizes plane wave pseudopotentials \[48\]. The phonon dispersions and the electron-phonon couplings are calculated within the framework of Density functional perturbation theory (DFTP) \[49\]. We choose the plane wave energy cut-off as 45 Ry and the charge density cut-off as 200 Ry. A Gaussian broadening of 0.02 Ry is used in our calculations. Phonon dispersions as well as electron-phonon coupling matrices were calculated on a \(4 \times 4 \times 2\) q-mesh grid. The electron-phonon coupling constant (\(\lambda\)) can be evaluated from the Eliashberg spectral function \([\alpha^2 F(\omega)]\) using the relation \([50, 51]\):

\[
\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (1)
\]

The Eliashberg spectral function is given by

\[
\alpha^2 F(\omega) = \frac{1}{2\pi N(\epsilon_F)} \sum \frac{\gamma_{qj}}{\omega_{qj}} \delta(\hbar \omega - \hbar \omega_{qj}). \quad (2)
\]

where \(N(\epsilon_F)\) is the electronic density of states at the Fermi level (\(\epsilon_F\)), \(\gamma_{qj}\) is the phonon linewidth due to electron-phonon scattering, \(\omega_{qj}\) is the phonon frequency with wave vector \(q\) and branch index \(j\). Superconducting transition temperature \((T_c)\) can be calculated for phonon mediated superconductivity from Allen and Dynes modified McMillan’s formula \([50, 51]\):

\[
T_c = \frac{\omega_{loq}}{1.2} \exp \left[ \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (3)
\]

where \(\omega_{loq}\) is the logarithmic average phonon frequency, expressed in Kelvin and \(\mu^*\) is the averaged screened electron-electron interaction. Debye temperature can also be estimated from elastic constants. Debye temperature can be written as \([52]\):

\[
\Theta_D = \frac{\hbar}{k_B} \left( \frac{3n}{4\pi} \frac{N_A \rho}{M} \right)^{1/3} \nu_m. \quad (4)
\]

where \(\hbar\) is Plank’s constant; \(k_B\) is Boltzmann’s constant; \(N_A\) is Avogadro’s number; \(\rho\) is density; \(M\) is the molecular weight; \(n\) is the number of atoms in the unit cell. The average wave velocity \(\nu_m\) approximately can be written as:

\[
\nu_m = \frac{1}{3} \left( \frac{2}{\nu_t} + \frac{1}{\nu_l} \right)^{-1/3}. \quad (5)
\]

where \(\nu_l\) and \(\nu_t\) are longitudinal and transverse elastic wave velocity related to bulk modulus (B) and shear modulus (G) as:

\[
\nu_l = \left( \frac{B + 4G/3}{\rho} \right)^{1/2}, \quad (6)
\]

\[
\nu_t = \left( \frac{G}{\rho} \right)^{1/2}. \quad (7)
\]

### III. RESULTS AND DISCUSSION

#### A. Elastic constants and mechanical stability

In the first step we relax all the atomic positions of ThFeAsN and ThNiAsN systems. For ThCoAsN, we perform full geometry optimization (both lattice parameters and atomic positions were relaxed). Using these relaxed structures, we calculate the elastic constants. All calculated elastic constants are presented in TABLE-III. All elastic constants are positive and obey the well-known Born criterion of mechanical stability \([53]\):

\[
C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, C_{11} - C_{12} > 0, C_{11} + C_{33} - 2C_{13} > 0, 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0.
\]

It is also evident from our calculations that the values of \(C_{33}\) of all the three systems are well above the limit of elastic stability i.e. \(C_{33} > C^* = 2C_{13}/(C_{11} + C_{12})\) \([54]\). For all the systems, we have \(B > G\), which indicates that the shear modulus \(G\) is the parameter that dictates the mechanical stability of the systems under consideration. From TABLE-III it is clear that the values of elastic constants and elastic modulus are very similar to that of the LaFeAsO system but not consistent with the previous theoretical calculation of ThFeAsN system \([37, 55]\). It turns out that the bulk modulus of these systems (~100 GPa) are smaller than that of the other classes of unconventional SCs like MgB\(_2\) (~122-161 GPa), YBCO (~200 GPa). Thus, in comparison to those unconventional SCs, ThXAsN (X=Fe,Co,Ni) are relatively soft materials with high compressibilities. Young’s modulus determine the stiffness of the materials. Therefore, ThFeAsN has the highest and ThCoAsN has the lowest stiffness. A material is considered to be brittle if it satisfies the well-known Pough’s criterion i.e. \(B/G < 1.75\). Our result indicate that ThFeAsN lies in the boundary of brittle and plastic state as that of the LaFeAsO compound. On the contrary, ThNiAsN and ThCoAsN systems clearly show plastic behaviour. The values of poisson’s ratios indicate the ionic nature of bonding in these three compounds.

#### B. Plasma frequency and effective dimensionality

Electronic structure calculations can provide important information about the effective dimensionality of a system through various implication like, dispersion-less (flat) energy bands along certain symmetry lines, van Hove singularities in density of states, etc. A simple quantitative estimate of the effective dimensionality can be acquired by calculating plasma frequencies along the various principle axes of the unit cell \([21]\). We evaluate the plasma frequencies of non-magnetic tetragonal ThX-AsN (X=Fe,Co,Ni) along different crystal axes and compared with other Fe based SCs including LaFeAsO (one of the parent compounds of 1111 family). In TABLE-III
we depict the ratio of the in-plane plasma frequency $\omega_p^d$ to the out-of-plane plasma frequency $\omega_p^p$ for various members of the Fe-based superconducting families. Along with that we also present some important structural parameters as well as superconducting transition temperature for some other Fe-based SCs. For all the representative compounds of different families of Fe-based SCs

as well as $d_{Fe-eFe}/d_{Fe-Fe}$ is very similar to that of the LaFeAsO. More 3D like electronic structure go against Fermi surface nesting, which may be the reason of not having spin density wave ordering like LaFeAsO system. On the other hand for Ni and Co systems, plasma frequency ratio is higher than that of the Fe system. This also indicate that these two systems posses a more 2D-like electronic structure as compared to the ThFeAsN. The ratio of shortest interlayer to the shortest intralayer Fe-Fe distance is $c/\sqrt{2}a$ for 122 system and $\sqrt{2}c/a$ for the others including the current studied systems. However, ThFeAsN violates the general trends of proportionality of $\omega_p^d/\omega_p^p$, to that of the $d_{Fe-eFe}/d_{Fe-Fe}$ for Fe-pnictides SCs. However, to understand the superconductivity and magnetism in these compounds, a rigorous electronic structure calculation is essential.

### C. Magnetism

In order to search for the theoretical magnetic ground state of ThXAsN (X=Fe,Co,Ni), we perform spin-polarized calculation for anti-ferromagnetic (AFM) as well as ferromagnetic (FM) spin configurations. We find that no magnetic ground state (AFM and FM) is stabilized in ThNiAsN. On the other hand, ground state of ThFeAsN is anti-ferromagnetic which is also consistent with the previous theoretical calculations [36, 39]. But experimentally no long range magnetic order was observed in this system [29]. Our calculation indicate that ground state of ThCoAsN is ferromagnetic. In TABLE-IV we summarize our results of magnetic calculations. In TABLE-IV we present the magnetic ground state energies of ThFeAsN and ThCoAsN systems with respect to the non-magnetic ground state energy of that system. We also evaluate the magnetic moment at Fe/Co/Ni, As atoms as well as total magnetic moment in the unit cell for ThFeAsN and ThCoAsN (see TABLE-IV). Magnetic moments at other atoms (Th and N atoms) are very

### TABLE II: Calculated elastic constants ($C_{ij}$), bulk modulus (B), shear modulus (G), Youngs modulus (Y) of ThX-AsN (X=Fe,Co,Ni) in GPa. Estimated values of Poisson’s ratios ($\nu$) and compressibilities ($\beta_H$ in GPa$^{-1}$) of ThXAsN (X=Fe,Co,Ni). Elastic constants ($C_{ij}$), bulk modulus (B), shear modulus (G) and Youngs modulus (Y) along with Poisson’s ratio ($\nu$) and compressibility for the LaFeAsO (a parent compound of 1111 Fe-based superconducting family) are also listed in the last column for comparison.

| System      | ThFeAsN | ThNiAsN | ThCoAsN | LaFeAsO |
|-------------|---------|---------|---------|---------|
| C$_{11}$    | 211.1   | 235.4   | 211.4   | 191.9   |
| C$_{12}$    | 73.6    | 76.2    | 63.7    | 55.9    |
| C$_{13}$    | 67.6    | 84.6    | 72.1    | 61.6    |
| C$_{33}$    | 104.5   | 119.7   | 109.4   | 144.8   |
| C$_{44}$    | 94.6    | 73.5    | 56.5    | 44.1    |
| C$_{66}$    | 39.2    | 55.7    | 44.2    | 77.9    |
| B$_H$       | 98.6    | 114.1   | 100.6   | 98.5    |
| G$_H$       | 60.7    | 59.8    | 50.6    | 56.5    |
| Y           | 151.1   | 152.8   | 130.1   | 141.5   |
| $\nu$       | 0.24    | 0.27    | 0.28    | 0.25    |
| $\beta_H$   | 0.0101  | 0.0087  | 0.0099  | 0.0102  |

*Reference [21]

### TABLE III: Ratio of the in-plane plasma frequency to the out-of-plane plasma frequency, c/a ratio, ratio of out-of-plane and in-plane Fe-Fe distance and superconducting transition temperature of various Fe-based SCs along with ThXAsN (X=Fe,Co,Ni).

| System      | $\omega_p^d/\omega_p^p$ | c/a | $d_{Fe-eFe}/d_{Fe-Fe}$ | $T_{max}^{P2a}$ (K) |
|-------------|-------------------------|-----|------------------------|---------------------|
| SrFeAsF$_x$ | 19.892                  | 2.2426 | 3.1715               | 56                  |
| LaFeAsO     | 8.9467                  | 2.1656 | 3.0626               | 55                  |
| FeSe        | 4.1119                  | 1.4656 | 2.0727               | 27                  |
| LiFeAs      | 3.2181                  | 1.6785 | 2.3738               | 18                  |
| BaFe$_2$As$_2$ & 3.2926 | 3.285 | 2.3228               | 38                  |
| ThFeAsN     | 3.0621                  | 2.1069 | 2.9797               | 35                  |
| ThCoAsN     | 6.3682                  | 2.06   | 2.9144               | 5.4                 |
| ThNiAsN     | 7.0934                  | 1.957  | 2.7683               | 4.3                 |

*Reference [55]

### TABLE IV: Ground state energy (with respect to non-magnetic state) and magnetic moments of ThFeAsN and ThCoAsN for different magnetic spin configurations. Density of states at Fermi level (N(E$_F$)) are also depicted in the table for different magnetic ground states along with the non-magnetic one. FM and AFM ground states are not stabilized in ThFeAsN and ThCoAsN systems respectively (not listed in the table).

| Order | ThFeAsN | ThCoAsN |
|-------|---------|---------|
| Energy(meV/f.u.) | -23.74 | -76.04 |
| N(E$_F$) | 0.006 (up) | 0.003 (dn) |
| (states/eV/f.u.) | 2.29 | 1.16 |
| Moment on Fe ($\mu_B$) | 1.39 | 0.58 |
| Moment on As ($\mu_B$) | 0.009 | 0.004 |
| Total Moment ($\mu_B$) | 0 | 0 |

*Reference [55]
FIG. 2: Calculated total (dotted line) and atom-projected density of states of (a)ThFeAsN (b)ThCoAsN (c)ThNiAsN systems for non-magnetic tetragonal phase. The Fermi energy is at 0 eV.

D. Electronic structure and spin-orbit coupling

Low energy electronic structure plays the key role in superconductivity. In this section we present our calculated electronic structures of ThXAsN (X=Fe,Co,Ni). In Fig.2 we have presented the atom-projected density of states for ThFeAsN, ThCoAsN and ThNiAsN compounds. Density of states at the Fermi level for the Fe and Co systems are quite higher than that of the Ni system. In ThCoAsN, a sharp peak in the DOS (mainly coming from Co atoms) at the Fermi level is observed. DOS at Fermi level (E_F) is important as it increases the possibility of electron-electron pairing which gives rise to superconductivity. The value of DOS at the E_F for ThFeAsN, ThCoAsN, ThNiAsN systems are respectively 2.29, 3.6 and 1.7 states/eV/f.u. In the Fe and Co systems, the projection of Fe/Co-d states is more than 75% of the total DOS (same in the Ni system is 35%) which makes these two compounds close to stoner instability [56, 57]. Our calculated DOS for ThFeAsN and ThNiAsN are in well agreement with that of the experiments as well as previous theoretical calculations [30, 36, 37, 39]. A closer look at Fig.2 reveals that there exists a pseudo-gap region at energy interval from 0.1 eV to 1 eV in ThFeAsN. This pseudo-gap region shrinks and shifts towards left as we move to the Co and Ni systems. In the Ni system, there is hardly any pseudo-gap region near Fermi level. As the number of electrons increases from the Fe to Ni systems, the chemical potential shifts towards right as we move from the Fe to Ni system. Shrinking of pseudo-gap region is related to the extent of the 3d orbitals of Fe, Co, Ni and its hybridization with the As-p orbitals. In Fig.3 we depict our d orbital-projected density of states for ThXAsN (X=Fe,Co,Ni). In the Fe system, d_{yz}, d_{xz} and d_{z^2} orbitals dominate the Fermi-level whereas in the Co system, Fermi level is mainly d_{xy} derived. In fact, a sharp peak in the density of states for Co 3-d_{xy} orbital is observed at the Fermi level. Lastly in the Ni system, no particular dominance of any particular orbital is observed. Overall, ThFeAsN and ThCoAsN show more multi-orbital characteristics near Fermi level than that of the ThNiAsN. Pseudo-gap like regions in the DOS (link to van Hove singularities) of ThFeAsN and ThCoAsN are mainly due to d_{z^2} orbitals which is extended along the c-axis (perpendicular to the Fe-Fe plane). This is also an indication of the influence of ‘anion height’ in the electronic structures of these two magnetic ground states of these systems are also shown in the TABLE 1 for comparison. Density of states at the Fermi level for ThFeAsN in the AFM phase is smaller than that in the non-magnetic phase. Density of states at Fermi level for ThCoAsN in the FM state is significantly smaller than that of the non-magnetic one. In the next section we discuss the electronic structures of ThXAsN (X=Fe,Co,Ni) for non-magnetic as well as stabilized magnetic ground states.

FIG. 3: Calculated orbital-projected [Fe-d_{xy} (red), d_{yz} (green), d_{xz} (blue), d_{z^2} (magenta), d_{x^2-y^2} (maroon), density of states of (a-d)ThFeAsN (e-h)ThCoAsN (i-l)ThNiAsN systems for tetragonal non magnetic phase.

close to zero (not listed in the table). We also report the density of states at the Fermi level for ThFeAsN and ThCoAsN systems in the AFM and FM ground states respectively. Density of states at Fermi level for non-
Since Co system possesses a very high DOS at the $E_F$, it is also very interesting to study the effect of doping (Co in place of Fe) in the superconducting properties of ThFeAsN. Next we will display our calculated band structures for ThXAsN ($X=$ Fe, Co, Ni) in the tetragonal non-magnetic phase. Fig. 4 depicts the band structures of ThXAsN (X=Fe, Co, Ni). We display our calculated orbital-projected band structures for ThFeAsN, ThCoAsN and ThNiAsN in the non-magnetic tetragonal crystal structure.

**FIG. 4:** Calculated band structures of (a)ThFeAsN, (b)ThCoAsN and (c)ThNiAsN in the non-magnetic tetragonal crystal structure.

**FIG. 5:** Calculated Fe (a) $d_{xz}$ (green), $d_{yz}$ (blue), (b) $d_{xy}$ (red), (c) $d_{z^2}$ (magenta) and (d) $d_{x^2-y^2}$ (brown) orbital-projected band structures of ThFeAsN.

**FIG. 6:** Calculated Fe (a) $d_{yz}$ (green), $d_{xz}$ (blue), (b) $d_{xy}$ (red), (c) $d_{z^2}$ (magenta) and (d) $d_{x^2-y^2}$ (brown) orbital-projected band structures of ThCoAsN.

**FIG. 7:** Calculated Fe (a) $d_{yz}$ (green), $d_{xz}$ (blue), (b) $d_{xy}$ (red), (c) $d_{z^2}$ (magenta) and (d) $d_{x^2-y^2}$ (brown) orbital-projected band structures of ThNiAsN.

**FIG. 8:** Calculated Fermi surface of (a)ThFeAsN (b)ThCoAsN (c)ThNiAsN. All FS pockets (hole and electron like) are shown separately for these three systems along with a number.
ThCoAsN and ThNiAsN systems in Figs. 6 and 7 respectively. Electronic band dispersions of Fe, Co and Ni systems, near the Fermi level are different from each other. But the band structure of ThFeAsN system is significantly different from the other two systems. Band structure of ThFeAsN is quite similar to the band structure of LaFeAsO (doped with F in O sites). On the other hand, band structure of ThCoAsN possess flat bands (less dispersive) near the high symmetry k points (Γ and M). Orbital characters of the bands near the Fermi levels are also different for all three systems. Calculated Fermi surfaces (FSs) of ThXAsN (X=Fe,Co,Ni) are depicted in Fig. 8. For Fe system FS consists of 3 hole like FSs at Γ point (0, 0, 0) and 2 electron like FSs at M (π, π, 0) points in the Brillouin zone. This Fermi surface topology of ThFeAsN is quite familiar with other Fe-based SCs including LaFeAsO [58, 59]. One hole like FS among three FSs at the Γ point is nearly two dimensional and consists of circular cylinder (k, dispersion is very less), whereas the electron like FSs at the zone corner (M points) are more 3D like. FSs calculated using experimental structural parameters, have some differences as shown in the appendix. For the Co and Ni systems, there are 3 electron like FSs around M point and 1 hole like FS at X point (no FS at Γ point). Since the appearance of FSs is at different points for ThFeAsN and ThCo(Ni)AsN, inter-band nesting vectors are different for these systems. These significant differences will affect the intra and inter-band nesting properties of this system which plays very important role in magnetism and superconductivity in these type of SCs. Absence of hole like FSs at the centre of the Brillouin zone (Γ point) in ThCoAsN and ThNiAsN does not help inter-band nesting of FSs. Hence these two systems not likely to show any density wave ordering. We also perform a Bader analysis of the charge densities for ThXAsN (X=Fe,Co,Ni), shown in TABLE V. A loss of 0.38 electrons in the [FeAs]− layer of ThFeAsN has been observed which is consistent with the previous theoretical study [32]. In case of ThCoAsN and ThNiAsN, we find a loss of 0.51 and 0.40 electrons in the [Co/NiAs]− layer respectively. In case of ThCoAsN, inter layer charge transfer is more as compared to the other two systems. Since theoretical magnetic ground state of ThFeAsN system is anti-ferromagnetic, we perform electronic structure calculations in AFM phase also. We present our calculated density of states band structures in the AFM phase for ThFeAsN in Fig. 9. It is quite obvious that, band structure in the AFM phase is different from the non-magnetic band structure. We present our calculated orbital-projected band structure of ThFeAsN in AFM phase in Fig. 10. It is evident from Fig. 10 that orbital character near the Fermi level is very similar to that of the non-magnetic one. On the other hand for ThCoAsN system, only FM ground states is stabilized. Therefore, we calculate the density of states as well as band structure of this system in the FM phase. In Fig. 11 we show our calculated density of states and band structures of ThCoAsN with ferro-magnetic spin configuration. Up and down spin density of states and bands are denoted by red and blue lines respectively.

FIG. 9: Calculated spin-polarised (a) Density of states and (b) band structures of ThFeAsN with anti-ferromagnetic spin configuration. Up and down spin density of states are denoted by red and blue lines respectively

FIG. 10: Calculated Fe (a) d_{yz} (green), d_{xz} (blue), (b) d_{xy} (red), (c) d_{z^2} (magenta) and (d) d_{x^2−y^2} (brown) orbital-projected band structures of ThFeAsN with anti-ferromagnetic spin configuration.

FIG. 11: Calculated spin-polarised (a) Density of states and (b) band structures of ThCoAsN with ferro-magnetic spin configuration.
our calculated band structures of ThXAsN (X=Fe,Co,Ni) including spin-orbit coupling (SOC) as denoted by blue lines. Calculated band structures of the same system without SOC is also depicted in the same figure for comparison. Spin-orbit coupling hardly make any impact in the low energy band structures of ThCoAsN and ThNiAsN systems. As we can see from Fig.12 in case of ThFeAsN the bands near Γ point are degenerate in absence of SOC, becomes non degenerate with the application of SOC. With spin-orbit coupling, the splitting of energy states at Γ is about 100 meV as compared to the splitting of 60 meV for FeTe system. This splitting of bands at Γ with SOC and the breaking of degeneracy can be roughly understood by the symmetry analysis. The site symmetry of the Fe atoms has twofold irreducible representation which breaks under SOC. It is quite evident from Fig.12 that the band at Γ point, predominantly $d_{yz}$ and $d_{xz}$ character splits into two bands with same mixed orbitals. Since in this system, there are no clear evidence of structural as well as magnetic transitions, no further splitting of $d_{yz}$ and $d_{xz}$ orbitals was observed. Moreover due to the presence of short range magnetic order as reported experimentally, in presence of local exchange splitting these $d_{x^2-y^2}$ ↑ orbitals in one site interacts differently with the $d_{x^2-y^2}$ ↓ orbitals in another site. This may lift the degeneracy of these two orbitals and produce orbital ordering as observed in other Fe-based superconductors having magnetic and/or structural transitions [61, 62]. These orbital ordering can be detect by transport, tunnelling and spectroscopy measurements. This orbital order may give rise to nematic order as suggested by Cao et al., in FeSe system [63]. However, nematic order in ThFeAsN system has not been studied experimentally. Presence of magnetic fluctuation along with this nematic order can be a driving mechanism of superconductivity in ThFeAsN system [63].

### E. Phonon dispersion and Electron phonon coupling

Now we discuss the lattice dynamical properties of ThXAsN (X=Fe,Co,Ni). Lattice dynamics of ThNiAsN have already been studied theoretically using DFPT [35]. In this work, we also present the phonon dispersion of ThNiAsN, calculated using PAW potential within DFPT whereas, previous calculation [35] has been done using ultra-soft pseudopotential (USSP). However, lattice dynamics study of ThFeAsN and ThCoAsN is not available in the current literature. In Figs.13a,14b and 15b, we present our calculated phonon dispersion relations for ThNiAsN, ThCoAsN and ThNiAsN systems respectively. For all three systems, the unit cell contains 8 atoms, there are 24 branches with three acoustic and 21 optical phonon branches. It is clear from these phonon dispersion relations that there are no imaginary frequencies in the phonon dispersion relations which make these systems dynamically stable. There exists a clear gap in the phonon dispersion relations in all the three systems. But the gap in Fe system is smaller than that of the Ni and Co systems. This difference is due to the atomic mass difference of Fe, Co and Ni atoms(Fe and Ni is heavier than Co). It is quite evident that, the higher frequencies of the optical branches are mainly due to the lighter N atoms and As atoms. On the other hand, the lower frequency manifold contains acoustic modes as well as mixed of both optical and acoustic modes, predominately comes from Th and Fe atoms. Phonon dispersion relation of ThFeAsN is not quite similar to that of the LaFeAsO where there is no gap between optical and acoustic modes [64]. Furthermore, we have studied the electron-phonon coupling and its influence in superconducting pairing in ThXAsN (X=Fe,Co,Ni). Fig.13a, Fig.14 and Fig.15b, we depict the phonon density of states (red) as well as Eliashberg spectral functions (blue) for ThNiAsN, ThFeAsN and ThCoAsN systems respectively. Our calculated phonon dispersion for ThNiAsN system is in well agreement with the previous theoretical calculation [35]. Our calculated electron phonon coupling constant $\lambda$ for ThNiAsN system is 0.45, which give rise to a $T_c$ of 1.7 K. However, previous calculation [35] using ultrasoft pseudopotential produce a $T_c$ of 3.4 K which is much closer to the experimental $T_c$ of 4.3 K. Our estimated value of electron phonon coupling constant $\lambda$ for ThFeAsN system is 0.31, which is

| Species | Bader analysis | Purely ionic |
|---------|----------------|--------------|
| ThFeAsN |                |              |
| Th      | 9.77           | 8 (Th$^{4+}$) |
| Fe      | 7.88           | 6 (Fe$^{2+}$) |
| As      | 5.73           | 8 (As$^{3-}$) |
| N       | 6.61           | 8 (N$^{3-}$) |
| ThN     | 16.38          | 16 (ThN$^{+}$) |
| FeAs    | 13.61          | 14 (FeAs$^{-}$) |

| Species | Bader analysis | Purely ionic |
|---------|----------------|--------------|
| ThCoAsN |                |              |
| Th      | 10.22          | 8 (Th$^{4+}$) |
| Co      | 8.99           | 7 (Co$^{2+}$) |
| As      | 5.49           | 8 (As$^{3-}$) |
| N       | 6.29           | 8 (N$^{3-}$) |
| ThN     | 16.51          | 16 (ThN$^{+}$) |
| CoAs    | 14.48          | 15 (CoAs$^{-}$) |

| Species | Bader analysis | Purely ionic |
|---------|----------------|--------------|
| ThNiAsN |                |              |
| Th      | 9.81           | 8 (Th$^{4+}$) |
| Ni      | 10.04          | 8 (Ni$^{2+}$) |
| As      | 5.56           | 8 (As$^{3-}$) |
| N       | 6.59           | 8 (N$^{3-}$) |
| ThN     | 16.40          | 16 (ThN$^{+}$) |
| NiAs    | 15.60          | 16 (NiAs$^{-}$) |
much lower than that of the ThNiAsN system (0.45). We have treated screened electron-electron repulsion $\mu$ as an empirical parameter and is varied from 0.10 to 0.15. Finally we use the Allen-Dynes-modified McMillan equation as mentioned earlier to obtain the superconducting transition temperature ($T_c$). Since ThNiAsN is an electron phonon mediated superconductor as established in the previous theoretical calculation [35] as well as our results, it is important to study the electron phonon coupling in ThFeAsN. But electron phonon coupling hardly playing any role in superconductivity as the experimental $T_c$ of ThFeAsN is over 30 K whereas theoretically, electron phonon coupling give rise to a $T_c < 1$ K. We also determine the electron-phonon coupling constant ($\lambda$) and superconducting transition temperature for ThCoAsN. In Table [V], we summarize our results of electron phonon calculations. Among all these three system, ThCoAsN has the highest $T_c$ and ThFeAsN has the lowest $T_c$ within the Eliashberg theory. Since DOS at Fermi level for ThCoAsN system is quite higher compared to the Fe system, electron-phonon coupling constant is also very high (0.65). This will give rise to a $T_c$ of 5.4 K. We also evaluate Debye temperature from elastic constants using the relations, mentioned in the computational method section. Debye temperature is related to average logarithmic phonon frequency ($< \omega^2 > \approx \Theta^2_D$). Fe system has the smallest logarithmic average phonon frequency $\omega_{log}$, whereas the values of average phonon frequencies $\omega_{log}$ for Co and Ni systems are almost same. $\alpha^2 F(\omega)$ is significantly arising from the lower frequency manifolds of the phonon bands for all three compounds. The number of phonon bands in the acoustic modes are more than that of the optical modes. It is quite evident from Figs [13b, 14b and 15b] that the magnitude of $\alpha^2 F(\omega)$ spectrum is highest in the case of Co system and lowest in the case of Fe system. As a consequence of

FIG. 12: Comparison of electronic band structures of (a)ThFeAsN, (b)ThCoAsN and (c)ThNiAsN with spin-orbit coupling (blue line) and without spin-orbit coupling (red line)

FIG. 13: (a) Phonon dispersion relation of ThNiAsN along the high symmetry directions of the Brillouin zone. (b) The Eliashberg spectral function $\alpha^2 F(\omega)$ (blue) and phonon density of states PhDOS (red) of ThNiAsN

FIG. 14: (a) Phonon dispersion relation of ThFeAsN along the high symmetry directions of the Brillouin zone. (b) The Eliashberg spectral function $\alpha^2 F(\omega)$ (blue) and phonon density of states PhDOS (red) of ThFeAsN
that, we find lowest electron phonon coupling constant for the Fe system and highest electron phonon coupling constant for the Co system (see TABLE VI). Moreover, Co system has very high DOS at the Fermi level as compared to the Fe and Ni systems. This is also a reason of getting a higher value of \( \lambda \) for ThCoAsN. Fig.2 shows that for Co and Fe systems, slight shift of Fermi levels (or chemical potential) change the DOS at \( E_F \) which in turn modify the electron-phonon coupling constants. This will effect the superconducting transition temperature significantly. In case of Ni system, slight shift of Fermi level, is not going to make any effect on DOS at \( E_F \). Next, we discuss the effect of AFM (SDW type) ground state on the electron-phonon coupling constant for ThFeAsN. It has been observed that electron-phonon coupling in Fe-based SCs is increased in presence of AFM background [20]. Further increment of electron-phonon coupling constant has also been shown by Coh et al. [18], when soft out of plane lattice vibrations are taken into accounts. According to Wong et al., we can write the effective electron-phonon coupling on Fermi surface as [38],

\[
\lambda_{eff} = \lambda_{F} R_{ph}^2 R_{SDW}^2 R_g^2.
\]  

Here, \( R_{ph} \) is the amplification factor due to out of plane soft lattice vibrations and it turns out to be 2 in AFM background [20]. \( R_{SDW} \) is the amplification factor due to SDW order which is also 2 [18]. \( R_g \) is the amplification due to the electrons scattered below Fermi surface which we ignore in our calculation. In case of strong coupling, renormalized effective electron-phonon coupling can be written as [38]:

\[
\lambda_{eff}^* = \frac{\lambda_{eff}}{\lambda_{eff} + 1}.
\]  

and renormalized screen electron-electron repulsion can be written as:

\[
\mu_{eff}^* = \frac{\mu_{eff}}{\mu_{eff} + 1}.
\]  

After employing all the amplification factors in \( \lambda \), we get an effective electron-phonon coupling constant \( \lambda_{eff} \) of 0.83 for ThFeAsN. This value of \( \lambda_{eff} \) give rise to a \( T_c \) of 15.3 K (with renormalized \( \mu \)). This value of \( T_c \) is still half the value of experimental \( T_c \).

**IV. CONCLUSIONS**

Summarising, our elastic constant calculations establish that, ThXAsN (X=Fe,Co,Ni) are mechanically stable. Our calculation reveals that ThFeAsN lies in the boundary of brittle and plastic behaviour which is very similar to that of the LaFeAsO system. On the other hand, Co and Ni systems show plastic behaviour. Calculated plasma frequencies of these three systems indicate that ThFeAsN system posses more 3D like electronic structure than that of the Co and Ni systems. Next we have presented a comparative study of electronic structures of ThXAsN (X=Fe,Co,Ni). DOS, band structure and FS for all these three systems have been studied systematically. Our calculations disclose that there are significant differences in the band structures and Fermi surfaces of these three compounds. Topology of Fermi surface of Ni and Co systems are quite similar whereas Fermi surface topology of Fe system is very similar to that of the LaFeAsO system. For Fe system, FS is mostly Fe \( d_{xz} \) and \( d_{yz} \) orbital derived, whereas for Co system, FS is dominated by \( d_{yz} \) orbital. We also found that for ThFeAsN, spin-orbit coupling significantly moderate the band structure near \( \Gamma \) point and give rise to a splitting of band (\( \sim 100 \) meV) and likely to influence superconducting and magnetic properties of the system. In case of ThCoAsN and ThNiAsN, low energy band structures remain unaltered with the introduction of spin-orbit coupling. Our phonon calculation firmly established that these three systems are dynamically stable as we found no imaginary frequencies in the phonon dispersion relations.
FIG. 16: Calculated band structures of non-magnetic ThFeAsN system using theoretical atomic position (red). Calculated band structures using fully experimental structural parameters (black lines) are also plotted for comparison.

We have also evaluated the superconducting transition temperatures within Eliashberg formalism for ThFeAsN and ThCoAsN systems for the first time. ThCoAsN have the highest \( T_c \) as calculated within the Eliashberg formalism among these three compounds that we studied. Our calculated \( T_c \) for ThFeAsN is very small (less than 1 K) as compared to the experimental \( T_c \) of 30 K. We find an significant enhancement in \( \lambda \) when AFM/SDW background and soft out of plane lattice vibrations in the layered structure are taken into consideration. Nevertheless, this amplification in \( \lambda \) (give rise to a \( T_c \sim 15 \) K) fail to produce the experimental \( T_c \) (30 K). This suggests that SC in ThFeAsN is more complicated and governed by low energy electronic structures. Further experimental and theoretical studies are required to understand the mechanism of SC in these systems particularly in ThFeAsN.

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VI. APPENDIX

In this appendix, we compare the band structures of ThFeAsN, calculated using the theoretical atomic positions (experimental lattice parameters and relaxed atomic positions) with the band structure calculated using experimental lattice parameters and atomic positions as shown in Fig.10. We observe that low energy band structure of ThFeAsN, using theoretical atomic positions clearly deviates from the band structure, obtained by using experimental lattice parameters. Our simulated Fermi surfaces (FSs) as depicted in Fig.17 also indicating the deviation. The number of FSs are also different in two cases as we can see from Fig.17. One noticeable difference in the FSs of ThFeAsN using geometry optimized atomic positions with the experimental one is the nature of FSs at \( \Gamma \) point. FSs around \( \Gamma \) point calculated employing experimental parameters is more two dimensional than that of the optimized one. These results are also consistent with the previous theoretical calculations [36, 39].

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