Pressure induced magnetic and structural transitions in ThMnAsN: An ab-initio study

Smritijit Sen and Houria Kabbour
Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois,
UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
(Dated: July 5, 2022)

In this work, we present first principles density functional study of magnetism and electronic structures of ThMnAsN at ambient as well as at high pressure. Magnetic ground state of ThMnAsN as resulted from our calculations, is C-type anti-ferromagnet which is consistent with the experiments. Our results also suggest that C-AFM ground states of ThMnAsN is insulating in nature with a small energy gap $\sim 0.4$ eV (using GGA exchange-correlation functional) at the Fermi level. Applying hydrostatic pressure in ThMnAsN, we find that all the structural parameters show anomalies at 9 GPa pressure which is attributed to a structural phase transition from tetragonal to collapse tetragonal phase. Apart from that our elastic constant and electronic structure calculations clearly show a increment in the metallic behaviour at higher pressure accompanying with a magnetic phase transition at the vicinity of 9 GPa pressure. We also observe that electronic structure of ThMnAsN at high pressure (9 GPa) closely resembles with the electronic structure of Fe-based superconductors.

I. INTRODUCTION

A plethora of ZrCuSiAs (1111) type compounds with diverse physical properties has been synthesized; largely because of the versatile nature of ZrCuSiAs type crystal structure in which all four crystallographic sites have a countless candidate elements to make it stable [1–4]. For instance, LaFeAsO which is the parent compound of first Fe based superconductor reported by Kamihara et al., posses ZrCuSiAs (1111) type structure consisting of alternative staking of [LaO$_2$Fe$_2$O$_3$]$^{2+}$ and [Fe$_2$As$_2$]$^{2-}$ layers with spin stripe type anti-ferromagnetic (AFM) order [4,5]. Superconductivity arises in this compound either by means of external pressure or by chemical doping (chemical pressure). However, a number of similar isostructural compounds with different physical properties has been reported. For example, LaCrAsO shows metallic anti-ferromagnetism [7]. On the other hand, LaMnAsO displays insulating anti-ferromagnetic behaviour [8]. Whereas, LaCoAsO is an itinerant ferromagnet in contrast to the Pauli paramagnetism with low temperature phonon mediated superconductivity in LaNiAsO [8] [12]. Mn based 1111 compounds including LaMnAsO in general, exhibit insulating behaviour with AFM ordering, which is of special interest because of its resemblance with the parent compounds of high $T_c$ cuprates superconductors. Apart from that, there are a number of Mn based compounds manifesting various phase transitions like Mott transition, charge ordering, spin reorientation transition etc., with the variation of temperature, external pressure, doping and applied magnetic field [13] [14].

In LaMnAsO, Sr doping in La site leads to a phase transition from AFM insulator to metallic AFM phase [14]. It is also reported that, AFM order in LaMnAsO can be fully suppressed by hydrostatic pressure yet no superconductivity has been discerned up to 1.5 K [21] [22]. However, there is no spin reorientation transition in LaMnAsO as observed in NdMnAsO, PrMnSbO, and CeMnAsO at low temperatures [16] [23] [24]. It is also worthy to be mentioned here that pressure induced metallization on the verge of metal-insulator transition is observed in BaMn$_2$As$_2$ experimentally along with the proclaimed superconductivity [25].

Recently, a new 1111-type Fe based superconductors ThFeAsN has been discovered with a superconducting $T_c$ as high as 30 K without external pressure or chemical doping [20]. Although no long range magnetic order has been found in ThFeAsN, a strong magnetic fluctuation above 35 K has been revealed via muon-spin rotation/relaxation and nuclear magnetic resonance techniques [27]. On the other hand, ThNiAsN is an electron-phonon coupled superconductor with a $T_c$ of 4.3 K as evident from the previous experimental and theoretical investigations [28,29]. However, a weak ferromagnetic ordering has been predicted theoretically in ThCoAsN [30]. ThMnAsN has been synthesized very recently by Zhang et al. and one common thing in all these ThZAsN (Z=Fe, Co, Ni, Mn) crystal structures is distinctively shorter c-axis in contrast to the other ZrCuSiAs (1111) type compounds which give rise to a inherent internal chemical pressure [31]. This internal in-built chemical pressure is believed to play an important role in the diverse physical properties of this series of materials. Neutron diffraction data suggests an AFM ordering in ThMnAsN at room temperature (300 K). Temperature variation of experimentally measured magnetic susceptibility exhibits cusps at 52 and 36 K respectively for ThMnAsN and ThMnP. This susceptibility cusps are indicating a spontaneous anti-ferromagnetic to anti-ferromagnetic transition for Mn$^{2+}$ moments as reported in the reference [31]. Ordered magnetic moments of ThMnAsN and ThMnP are 3.41 $\mu_B$ (2.30 $\mu_B$) and 3.60 $\mu_B$ (2.69 $\mu_B$) respectively, measured at 4 K (300 K) [31]. The range of values of Mn moments can be well understood in terms of the half-filling of Mn-3d orbitals, which maximizes Hund’s coupling and the reduction of moment from the full moment of gS = 5 $\mu_B$ is due to the valence fluctuations [22]. An extensive investigation revealing the structural

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parameters like bond length, bond angle and electronic structure is required to understand the physical properties of ThMnAsN. Recent experimental as well as theoretical studies on ZrCuSiAs (1111) type compound reveal that the electronic structure is very sensitive to pressure (chemical/external) \(^{22, 31, 32}\). Therefore, it is very interesting to study the effect of external pressure on the magnetism and electronic structures of ThMnAsN.

In this work, we systematically study the magnetism and electronic structures of ThMnAsN at ambient pressure. Our theoretical results quantitatively explain most of the experimental findings of ThMnAsN \(^{31}\). We also investigate the effect of hydrostatic pressure on the structural and physical properties of ThMnAsN. Our calculations also suggest that at higher pressure, ThMnAsN posses very similar electronic structure as that of the Fe based superconductors.

**II. COMPUTATIONAL METHODS**

The crystal structure of ThMnAsN is tetragonal with space group symmetry \(P4/nnm\) (space group no. 129). ThMnAsN consist of alternating layers of MnAs and ThN. MnAs plane is very similar to the FeAs/Se plane of the Fe based superconductors where Mn atoms are in the same plane but the As atoms are situated above and below of that plane. Height of this As atoms from the Mn plane is known as ‘anion height’. Experimental lattice parameters of tetragonal ThMnAsN at 4 K, are used as the input of our first principles density functional theory calculations \(^{31}\). Our first principles calculations were performed by employing the projector augmented-wave (PAW) method as implemented in the Vienna \(ab\ ini\textit{tio}\) simulation package (VASP) \(^{33–35}\). Exchange correlation functional has been treated under generalized-gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) functional \(^{36}\). We consider four magnetic spin arrangements namely ferromagnetic (FM), C type anti-ferromagnetic, A type anti-ferromagnetic and G type anti-ferromagnetic for magnetic Mn atoms as shown in Fig.\(1\). We construct a \(\sqrt{2} \times \sqrt{2} \times 2\) super-cell in order to implement the above mentioned spin arrangements. A schematic diagram of \(\sqrt{2} \times \sqrt{2} \times 2\) super-cell of ThMnAsN is shown in Fig.\(2\). Various magnetic coupling constants \((J_1, J_2, J_3)\) are also indicated in the Fig.\(2\). We perform a spin polarised single point energy calculation using various spin configurations as mentioned above. The wave functions were expanded in plane waves basis with an energy cutoff of 550 eV and the energy tolerance of self consistence calculations are set to \(10^{-6}\) eV. The sampling of the Brillouin zone was done using a \(\Gamma\)-centered \(6 \times 6 \times 3\) Monkhorst-Pack grid. To obtain the crystal structures at different pressures, we start with \(P=0\) structure. Then, we increase the pressure gradually at the steps of 1 GPa and relax the lattice parameters and internal atomic coordinates at each pressure. Density of states calculations are performed using these optimized crystal structures at a particular external pressure. The forces and stresses of the converged structures at each pressure were optimized and checked to be within the error allowance of the VASP code. Elastic constants were calculated within VASP by finite differences of stress with respect to strain \(^{38}\). For the Fermi surface calculations in the non magnetic phase, a denser k-grid of size \(20 \times 20 \times 20\) is considered for the calculation. In order to visualise the Fermi surface, we use
Fermi surfer software [39]. Charge density plots are prepared using VESTA software [40]. The COHP (Crystal Orbital Hamilton Population) analysis was carried out in the framework of the LOBSTER software [41–43].

III. RESULTS AND DISCUSSION

A. Magnetism and electronic structure

First, we find the magnetic ground state of the tetragonal ThMnAsN. As mentioned earlier, we consider three different anti-ferromagnetic (AFM) spin arrangements along with the ferromagnetic (FM) spin configuration (see Fig.1). In order to find the magnetic ground state, we perform single point energy calculations using the experimental lattice parameters as well as atomic positions for various spin configurations namely FM, C-AFM, A-AFM and G-AFM. In Table-I, we depict our calculated total energies and local magnetic moments of Mn atoms of ThMnAsN for NM, FM, A-AFM, C-AFM and G-AFM spin configurations. It turns out that C-AFM spin arrangement has the lowest total energy among all other spin arrangements that we considered. Therefore, ThMnAsN have C-AFM type ground states which is consistent with the experimental findings [31]. From Table-I, we can clearly see that magnetic moments in Mn atoms are 3.52 $\mu_B$ for ThMnAsN with C-AFM spin configuration. Magnetic moments in Mn atoms as well as total energy for C-AFM and G-AFM spin arrangements in ThMnAsN are quite similar but differ significantly from that of the A-AFM and FM spin arrangements. Our calculated ground state Mn moments (C-AFM spin configuration) for ThMnAsN, is quite close to that of the experimental one (measured at 4 K). We present our calculated density of states (spin-polarised) of ThMnAsN in Fig.3 for all four magnetic spin arrangements. It is quite evident from Fig.3 that in case of C-AFM and G-AFM spin configuration, both of these systems posses a small energy gap in the density of states at the Fermi level (insulating behaviour at low temperature). On the other hand, for the other two spin configurations (A-AFM and FM), density of states clearly suggest a metallic behaviour for ThMnAsN.

B. Effect of hydrostatic pressure on the crystal structure and magnetism of ThMnAsN

In this section, we will demonstrate the effect of hydrostatic pressure in the structural parameters, magnetism and electronic structures of ThMnAsN. In the first step, we fully optimize (both lattice parameters as well as atomic positions) the geometry of the crystal structure. In Table-II, we present the GGA optimized structural parameters as well as the local magnetic moment of Mn for ThMnAsN with the C-AFM spin arrangement.

| Structural parameters | GGA (C-AFM) | Experiment* (4 K) |
|-----------------------|-------------|-------------------|
| a=b (Å)               | 4.084       | 4.076             |
| c (Å)                 | 8.297       | 8.297             |
| V (Å³)                | 148.89      | 148.34            |
| $z_{Th}$              | 0.1293      | 0.1291            |
| $z_{As}$              | 0.6631      | 0.6627            |
| Mn moment ($\mu_B$)   | 3.42        | 3.41              |

* Reference [31]
K in Table III (last column). Changes in the optimized lattice parameters with the experimental values are less than 0.2 % whereas 1.4 % decrease in the \(Z_{\text{As}}\) value is observed. On the other hand, local magnetic moment of Mn in the optimized structure is in good agreement with the experimentally measured value. It should be noted that the value of local magnetic moment of Mn atom in ThMnAsN with C-AFM spin configuration, calculated using experimental structural parameters is 3.52 \(\mu_B\). To obtain the crystal structures at various pressures, we begin with the optimized structure at \(P=0\) (Table III). In the next step, we optimize the lattice parameters as well as atomic positions in presence of hydrostatic pressure and we increase the external pressures in the steps of 1 GPa. In Fig 4, we display the variation of various structural parameters like normalized lattice parameters \((a/a_0, c/c_0)\), \(c/a\) ratio, volume of the unit cell \((V)\) and local magnetic moment of Mn atom with hydrostatic pressure in ThMnAsN with C-AFM spin configuration.

At 9 GPa pressure as compared to the Mn-Mn bond distance. Added to that, Fig 5c, showing the variation of in-plane and out of plane As-As distances (‘anion height’) with pressure also indicate a significant out of plane modification (along the c-axis) that occurs at 9 GPa pressure. Modifications of Mn-As tetrahedral bond angles (\(\alpha\) and \(\beta\)) are depicted in Fig 5. In all these figures (Fig 5b-d), we also depict the schematic diagrams of in plane and out of plane As-As distances, anion height, As-Fe-As tetrahedral bond angles in the inset. It is quite evident from Fig 5d that, a large distortion in the Mn-As tetrahedron transpire at 9 GPa pressure. Therefore, we can say that crystal structure plays a crucial role in controlling the physical properties of ThMnAsN system.

Next we present the variation of elastic constants of tetragonal ThMnAsN as a function of hydrostatic pressure as depicted in Fig 6. It shows that all the elastic constants are more or less increasing with the increase of external pressure except \(C_{44}\). It is also to be noted here that elastic constant \(C_{11}\) is always greater than \(C_{33}\).
up to 15 GPa pressure which indicates that it is easier to compress the system along 001 direction than to 100 direction. In order to understand the observed behaviour of elastic constants around 9 GPa pressure, we also calculate the Cauchy pressure for tetragonal system as a function of pressure (see Fig. 6b). It is well known that for metallic bonding, the Cauchy pressure is positive, while for directional bonding, it is negative and larger negative Cauchy pressure indicates a more directional character in the bonds \[45\]. As we can see from Fig. 6b, Cauchy pressure \( C_{13}-C_{44} \) has small negative value at lower pressure but it increases rapidly as we go above 9 GPa pressure. On the other hand, there is almost no variation of Cauchy pressure \( C_{12}-C_{66} \) with the hydrostatic pressure. This is so, because the variations of elastic constants \( C_{12} \) and \( C_{66} \) with the pressure are not very substantial as compared to the other elastic constants where the pressure variation is noticeable. High positive values of Cauchy pressure \( C_{13}-C_{44} \) above 9 GPa pressure indicate the enhancement of metallic behaviour.

In Fig. 7, we present the pressure variation of \( C_{44} \). There is a sudden drop of \( C_{44} \) at around 9 GPa pressure and above 14 GPa pressure \( C_{44} \) becomes negative. When the value of \( C_{44} \) is less than zero, it indicates that the system is mechanically unstable or is on the threshold of structural phase transition. Further we have also depicted the charge densities of ThMnAsN at various pressures along the 100 plane in Fig. 9. We can clearly see that (see the black arrow in the Fig. 9) at 9 GPa pressure, the overlap of charge densities along Mn-As bond is significantly increased if we compare the same with that at the 8 GPa pressure.

All these results collectively stipulate the enhancement of metallic character above 9 GPa pressure. To corroborate the charge density plots at 1, 8, and 9 GPa, the calculated integral crystal orbital Hamilton population (ICOHP) is indicated on Table III. Their sign indicates net bonding for the reported distances. The absolute value of the ICOHP is proportional to the strength of the bond and is increasing for all bonds with pressure from 1 to 9 GPa. The Mn-As absolute value shows an increase of 6.7 % from 1 to 8 GPa and of 8.9 % from

![FIG. 7: Variation of \( C_{44} \)-P as a function of external pressure for tetragonal ThMnAsN.](image)

![FIG. 8: Calculated density of states of ThMnAsN with C-AFM spin configuration at (a) 1 GPa, (b) 5 GPa, (c) 8 GPa and (d) 9 GPa pressure. Fermi level is denoted by a vertical black line at \( E = 0 \) eV.](image)

![FIG. 9: Calculated charge density plots of ThMnAsN along (100) plane at (a) 1 GPa, (b) 8 GPa and (c) 9 GPa of hydrostatic pressure.](image)
8 to 9 GPa, considering the up spin channel (similar trend is observed for the down spin channel). Therefore, the evolution in the smaller range 8 to 9 GPa is more important than the whole 1 to 8 GPa range. It pictures the structural transition described from 8 to 9 GPa and the greater metallic character at 9 GPa. The projected COHP on another hand is shown on Fig. 10 for the bonds Mn-As. Antibonding states are present at the top of the valence band just below the Fermi level for both 1 and 8 GPa. In the two later the band gap is opened in the AFM state while the metallic state at 9 GPa gives rise to antibonding states at the Fermi level. Such situation is destabilizing and should lead to a structural distortion and/or magnetic transition. Now we present our calculated density of states at different hydrostatic pressures (see Fig. 11). We can clearly see, with the increasing pressure metallic behaviour is increasing. This suggests that ThMnAsN is in the threshold of a metal insulator transition and this transition may occur with the variation of pressure, temperature or may be even with the doping. However, in this work, we have not studied the effect of doping and temperature in ThMnAsN. Nevertheless, we find three possible phase transitions (AFM to PM, tetragonal to collapse tetragonal and insulator to metal) that take place at around 9 GPa pressure. However, further experimental and theoretical studies are required to understand the interrelation between these phase transitions in ThMnAsN.

C. Electronic structure of ThMnAsN at high pressure

In this section, we will present the electronic structure of non magnetic ThMnAsN at 9 GPa pressure and discuss the possible manifestation of high temperature superconductivity. We clearly see that at 9 GPa pressure, an anti-ferromagnetic to para-magnetic transition occurs in ThMnAsN. Therefore, we perform a non spin polarized calculation to find the electronic structure of ThMnAsN in the non magnetic phase at 9 GPa pressure. In Fig. 11, we display our calculated atom projected density of states. Atom projected density of states suggest...
the Fermi level. Therefore, Mn d-orbital projected density of states for non magnetic ThMnAsN at 9 GPa pressure is presented in Fig.13b. All five Mn-d orbitals are present at the Fermi level. Among them, Mn \( d_{xz+y^2} \) orbitals dominate the Fermi level. In Fig.12 we depict our calculated band structure of non magnetic ThMnAsN at high pressure (9 GPa). Positions of Fermi level at different chemical potentials are also indicated in the band structure with a dotted line which is used to mimic the electron doping in the non magnetic ThMnAsN system within the rigid band model. With the value of chemical potential (\( \mu \)) 0.25, we find a electronic band dispersion very similar to that of the generic band dispersion of Fe based superconductors. We also find that orbital nature of the low energy bands of electron doped ThMnAsN (within rigid band approximation with \( \mu = 0.25 \)) at 9 GPa pressure which are also quite similar to the low energy band dispersion of most of the Fe based superconductors. In Fig.13 we depict the Mn d-orbital projected density of states and charge density plots. Moreover, we have seen a significant increase of positive Cauchy pressure \( C_{44} \) with increasing pressure, metallic behaviour of the system also enhances around 9 GPa pressure, also indicating an abrupt uplift of the metallic character in ThMnAsN. Therefore, we find that local magnetic moments of Mn atoms also collapsed at 9 GPa pressure indicating a magnetic phase transition from a tetragonal to a collapse tetragonal phase. We find that all the structural parameters show anomalies at 9 GPa pressure which is attributed to a structural phase transition from AFM to PM phase. We also evaluate the variation of various elastic constants of tetragonal ThMnAsN with pressure. We show that with the increasing pressure, metallic behaviour of the system also enhances which is supported by our pressure dependent density of states and charge density plots. Moreover, we have seen a significant increase of positive Cauchy pressure \( C_{44} \) around 9 GPa pressure, also indicating an abrupt uplift of the metallic character in ThMnAsN. Therefore, we find that local magnetic moments of Mn atoms also collapsed at 9 GPa pressure indicating a magnetic phase transition from a tetragonal to a collapse tetragonal phase.

IV. CONCLUSIONS

In this section, we briefly summarise our results. Through our first principles calculations, we find the magnetic ground state of ThMnAsN and it turns out to be anti-ferromagnetic with C type spin orientation. Our results are in good agreement with the experimental findings [31]. A small energy gap (~ 0.4 eV) is observed in the density of states near Fermi level. Applying hydrostatic pressure in ThMnAsN, we find that all the structural parameters show anomalies at 9 GPa pressure which is attributed to a structural phase transition from a tetragonal to a collapse tetragonal phase. We find that local magnetic moments of Mn atoms also collapsed at 9 GPa pressure indicating a magnetic phase transition from AFM to PM phase. We also evaluate the variation of various elastic constants of tetragonal ThMnAsN with pressure. We show that with the increasing pressure, metallic behaviour of the system also enhances which is supported by our pressure dependent density of states and charge density plots. Moreover, we have seen a significant increase of positive Cauchy pressure \( C_{44} \) around 9 GPa pressure, also indicating an abrupt uplift of the metallic character in ThMnAsN. Therefore, we

| Pressure(GPa) | Mn-As(Å) | ICOHP(up/dn) | Th-N(Å) | ICOHP(up/dn) | Th-As(Å) | ICOHP(up/dn) |
|--------------|----------|--------------|---------|--------------|----------|--------------|
| 1            | 2.508    | -3.89/-3.52  | 2.347   | -2.69/-2.68  | 3.417    | -1.47/-1.49  |
| 8            | 2.449    | -4.15/-3.74  | 2.316   | -2.80/-2.80  | 3.291    | -1.66/-1.68  |
| 9 (AFM)      | 2.336    | -4.52/-4.16  | 2.309   | -2.84/-2.84  | 3.281    | -1.84/-1.86  |
| 9 (NM)       | 2.336    | -8.74 (-4.37/spin channel) | 2.309  | -3.69 (-2.84/spin channel) | 3.281    | -3.65 (-1.83/spin channel) |

**TABLE III: ICOHP (Integral Crystal Orbital Hamilton Population) for ThMnAsN for the different types of bonds at pressures of 1, 8 and 9 GPa.**
observe a simultaneous structural, magnetic and metal-insulator transitions that occur at the vicinity of 9 GPa pressure. Electronic structure of ThMnAsN at high pressure closely resembles with the electronic structure of Fe-based superconductors. Therefore, a possible unconventional high temperature superconductivity may appear in ThMnAsN which might help to resolve the unsettled issues of Fe based superconductivity or in general high temperature superconductivity. However, further experimental and theoretical studies are required to understand the physical properties of ThMnAsN.

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