Electronic Structure and Structural Phase Transition of $EuCo_2As_2$ under Pressure

R.Mahesh, T.Gnanapongothai, B.Rameshe, U.Reka and B.Palanivel

Abstract—the electronic structure and structural phase stability of $EuCo_2As_2$ compound is studied using the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method implemented in WIEN2K. To study the structural stability and phase transition, the total energies of this compound have been computed as a function of reduced volumes and fitted with Brich Murnaghan equation. The estimated lattice parameters are in good agreement with available experimental data. The present theoretical calculations reveal that $EuCo_2As_2$ undergo a structural phase transition from Tetragonal phase into Collapsed Tetragonal phase under pressure at about 4.0 GPa. The estimated phase transition parameters are in good agreement with recent experimental data.

Index Terms— Electronic Structure, Ab initio calculations, Structural phase transition, High pressure, Superconductors.

1 INTRODUCTION

The discovery of superconductivity in iron pnictides [1] has initiated an enormous amount of activities related to these materials. The pnictides $REFe_2As_2$ (RE = rare earth, alkaline earth), which form in the tetragonal $ThCr_2Si_2$ ("122") - type structure, are one class of materials which exhibit superconductivity under appropriate chemical-doping or under the application of external pressure. $EuFe_2As_2$ is a member of the "122" family and exhibits superconductivity under the application of 2-3 GPa pressure [2]. This family (122) undergoes an isostructural phase transition from tetragonal to collapsed tetragonal phase which is accompanied by anomalous compressibility effects [3], [4], [5]. Studies on 122 phosphide systems have been carried out and isostructural transitions from tetragonal to collapsed tetragonal accompanied by negative compressibility axial properties have been reported in ternary phosphides under pressure [6], [7] and in other compounds [8].The experimental observation of pressure induced isostructural phase transition accompanied by an abnormal increase in the a-axis and drastic decreases in c-axis. The $CaFe_2As_2$ (122 family) at ambient pressure undergo phase transition from a tetragonal to an orthorhombic phase at 172 K accompanied by a magnetic transition [9].At low temperatures, when the pressure is above 0.35 GPa, the orthorhombic structure of $CaFe_2As_2$ transform to a collapsed tetragonal structure but no signature of superconductivity[10]. The electronic band structure calculation on $CaFe_2As_2$ system such structural phase transitions strongly affect the electronic structure of this system is reported by T.Yildiriym et al [11].

The occurrence of both pressure induced superconductivity and isostructural (tetragonal [T] to collapsed tetragonal [cT]) phase transition accompanied by extremely anisotropic and negative compressibility axial phenomenon in which the a axis length increases while the c axis length decreases under pressure has also been reported in the ternary 122-type iron-pnictide superconductors $EuFe_2As_2$,$BaFe_2As_2$[5], and $CaFe_2As_2$[12].

The negative compressibility phenomenon is suggested to be a common phenomenon in other iron-based superconductors of type AT_2As_2 (A = Ba, Eu, Sr, Ca and T = Fe, Co).Very recently Magnetic properties and superconductivity of $EuCo_2As_2$ compound (Fe atoms are replaced by Co atoms in $AeFe_2As_2$ materials) have been studied by J Ballinger et al [13]. They found that the magnetic structure for FM interactions combined with the appearance of the antiferromagnetic ordering and the anisotropic magnetic behavior at lower temperature suggest a magnetic structure in which the Eu^{2+} spins most likely align ferromagnetically with in the a-b plane and antiferromagnetically along the c-axis. The Eu^{2+} spin of single crystal $EuCo_2As_2$ is of an A-type AFM structure below 39 K. These magnetic characterizations are similar to those of $EuFe_2As_2$, and there is no evidence for a Co^{2+} magnetic moment. The valence fluctuation to have an influence on magnetic phase transitions at low temperatures and have an overall effect on structural phase transitions under high pressure at room temperature due to enhanced compressibility that accompanies valence fluctuations. Matthew Bishop et al [14] studied the structural properties of $EuCo_2As_2$ up to 35 GPa, using high pressure XRD in a diamond anvil cell. They found that $EuCo_2As_2$ undergoes a structural phase transition to a "collapsed tetragonal phase" (cT-pahse) under pressure in which the a-parameter increases from 3.9671Å to 4.0615**Å** and c-parameter reduced from 11.0632**Å** to 10.0510**Å**. The anomalous compressibility of the **a** axis continue until 4.7GPa. This interesting report motivated the present study on $EuCo_2As_2$ using first-principles calculations.

With the increase of computational power, *ab initio* calculations become a powerful tool in understanding the electronic band structure and structural phase stability of materials. This paper deals with the theoretical investigation of high pressure

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phase transition of $EuCo_2As_2$ from tetragonal phase (*I*4/mmm) to collapsed Tetragonal (I4/mmm).The next section describes the method of calculation. The third section presents the Crystal Structure details. The fourth section describes the structural phase stability. The fifth section gives the result and discussion and last section is devoted to conclusion.

2 Method of Calculation

The linearized augmented plane wave (LAPW) method is one of more the accurate methods for performing electronic structure calculations. It is based on the density functional theory for the treatment of exchange and correlation and uses the local spin density approximation (LSDA). But recent improvements using the generalized gradient approximation (GGA) gives better results for electronic structure calculations for crystals. In this work the electronic structure calculation of $EuCo_2As_2$ compound was calculated using the full potential linearized augmented plane-wave (FP-LAPW) method implemented in WIEN2K [15] within the generalized gradient approximation (GGA) to the exchange-correlation potential according to the Perdew-Burke-Ernzerhoff parameterization [16]. In the present calculation of $EuCo_2As_2$ compound the valence electrons of Eu ($4f^7\ 5d^0\ 6s^2$) orbital, Co ($3d^7\ 4s^2$) states and As ($3d^{10}\ 4s^2\ 4p^3$) states are treated with generalized gradient approximation (GGA). The muffin tin radii were chosen as 2.5 a.u, 2.32 a.u for Eu, Co and 2.05 a.u for As in the Tetragonal (I4/mmm) phase whereas for Collapsed tetragonal phase(I4/mmm) the muffin tin radii were chosen as 2.5 a.u,2.18 a.u for Eu, Co and 1.93 a.u for As. The Brillouin zone sampling was performed according to the Monkhorst-Pack scheme. 1000 k points in the entire Brillouin zone were used for k-space integration for both phases of $EuCo_2As_2$. The number of plane waves in a Fourier expansion of potential in the interstitial region was restricted to $R_{MT} \times k_{max} = 7$. The total energy calculations the energy convergence criterion was set to 10^{-6} Ryd for both ambient and high pressure tetragonal phases.

3 Crystal Structure of $EuCo_2As_2$

At room temperature, $EuCo_2As_2$ crystallize in the $ThCr_2Si_2$ structure (space group I4/mmm) as shown in Figure 1. The unit cell has two formula units. The experimental lattice parameters are a = b = 3.9671 **Å** and c = 11.063 **Å** [14]. The atomic positions for space group I4/mmm: Eu (2a) (0 0 0), Co (4d) (1/2 0 1/4), and As (4e) (0 0 z_{As}), where z_{As} is the internal parameter. Present calculations reveal that variation of z_{As} as a function of pressure is not appreciable; hence the experimental value of internal atomic parameter z_{As} is used throughout the calculation. The high pressure phase of collapsed tetragonal structure (cT) is also having the same phase group but with larger a=b=4.0615 **Å** and smaller c=10.0510 **Å** lattice parameters. $EuCo_2As_2$ basically exhibit Body centered tetragonal symmetry (I4/mmm) at ambient condition. In order to estimate the equilibrium lattice parameters of $EuCo_2As_2$ in BCT (I4/mmm) as well as for cT phase, the total energies are calculated as a function of volume and fitted with the Birch Murnaghan equation [17]. The estimated lattice parameters are given in Table.1 along with the available experimental values.

TABLE .1

Estimated Equilibrium Lattice parameters a(Å) and c(Å) of T and cT phases of $EuCo_2As_2$.

Structure	Lattice parameter	
	a (Å)	c(Å)
Tetragonal	3.9404 3.9671[a]	10.9834 11.063[a]
Collapsed Tetragonal	4.0546 4.0615[a]	10.0340 10.0510[a]

[a] Expt[14].

The calculated bulk modulus of $EuCo_2As_2$ in tetragonal phase is 63.68 GPa (48±4GPa) and that of collapsed tetragonal phase is about 93 GPa (111±2GPa). The experimental observation of increasing trend in bulk modules from normal to high pressure phase of $EuCo_2As_2$ is also obtained in the present calculations.

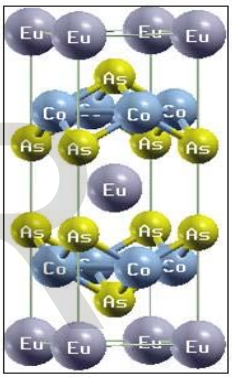

Fig. 1. Crystal Structure of $EuCo_2As_2$

The *c*/*a* ratio in the tetragonal and collapsed tetragonal phases are optimized by total energy minimization and it is found to be 2.70 **Å** and 2.40 **Å** for both phases which are in good agreement with the experimental value [14]. The *c* /*a* minimization for tetragonal and collapsed tetragonal phases are shown in Figure 2.

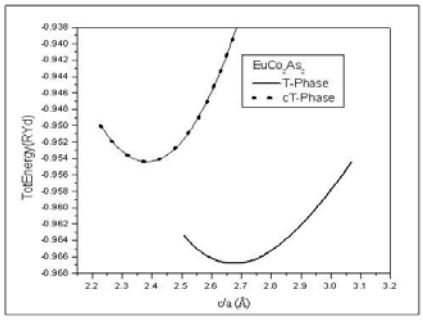

Fig. 2. c/a optimization curve for T and cT phases of $EuCo_2As_2$

4 Structural Phase Stability

In order to study the structural phase stability of $EuCo_2As_2$, the total energies are calculated in a manner similar to our earlier works [18], [19] for Tetragonal and collapsed tetragonal structures by reducing volume from 190 **Å** to 140 **Å**. The variations of the total energies with relative volume for both phases of $EuCo_2As_2$ compound are given in Figure 3. From the graphs, it can be clearly seen that tetragonal phase is more stable at normal pressure; however it undergo structural phase transition to collapsed tetragonal structure under pressure.

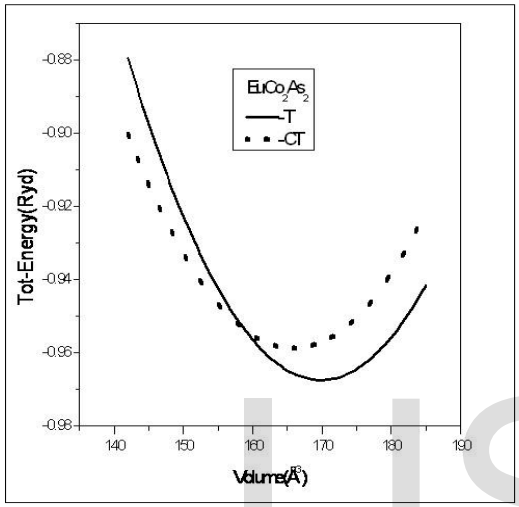

Fig.3. Variation of Total Energy (per formula unit) versus Volume for T and cT phases of $EuCo_2As_2$.

The calculated total energies are fitted to the Birch equation of state [20] to obtain the pressure volume relation. The EOS graphs connecting the pressure and relative volume in tetragonal and collapsed tetragonal phases are shown in Figure 4. The pressure is obtained by taking the volume derivative of the total energy. The bulk modulus is also calculated from the P–V relation

$$B=-V_0\, dP/dV \qquad (1)$$

The structural phase stability is determined by calculating Gibb's-free energy (*G*) [20] for tetragonal and collapsed tetragonal structures, which is

$$G=E_{tot}+PV-TS \qquad (2)$$

Since the theoretical calculations are performed at 0 K

$$H=E_{tot}+PV \qquad (3)$$

At a given pressure a stable structure is one for which enthal py has its lowest value and the transition pressures are calcu lated at which the enthalpies for the two phases are equal. The high-pressure behavior of $EuCo_2As_2$ is as follows: the transition from tetragonal and collapsed tetragonal occur around 4 GPa with a volume collapse of 2.5%, which are comparable to experimental transition pressure 4.7 GPa and volume collapse of 3.8 %.

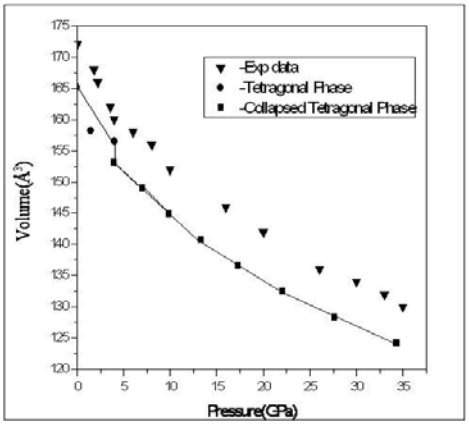

Fig.4. Equation of State of $EuCo_2As_2$

The phase transition pressure can be obtained by matching enthalpies of both structures such that the difference of enthalpy becomes zero. i.e. ($\Delta H=H_{B2}-H_{B1}=0$) at transition pressure. The phase transition pressure (4.0 GPa) reported in this work agrees well with the available experimental value (4.7 GPa) [14] shown in Figure 5.

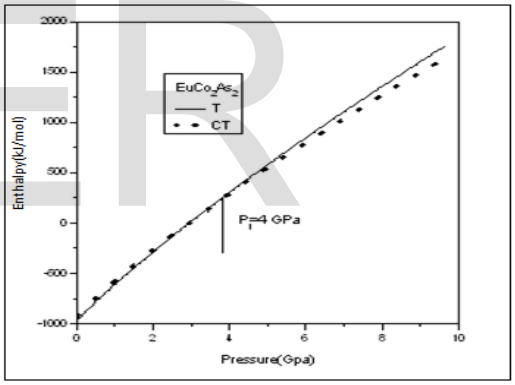

Fig. 5. Estimation of the phase transition from Tetragonal to Collapsed tetragonal structure

5 Result and Discussion

The electronic band structure calculation and bonding analysis are important for isostructural phase transition to get a better understanding of the cT-phase. It is well known that ferromagnetic interactions with the appearance of antiferromagnetic ordering suggest that Eu spin align antiferromagnetically along c-axis. Present calculations also reveals that AFM ordering is more stable compared to FM ordering. Figures .6 show the electronic band structure of tetragonal and that of collapsed tetragonal structure. In collapsed tetragonal phase show that despite to the 0.89 Å c- axis reductions, the band structures of both phases are similar. The main difference between the two phases is that most of the bands are shifted in lower energy in the cT-phase which is expected since the cT-phase has the lower energy. This downward shift

of the bands is most obvious in the band structure plot along the M-Z-X-P direction as shown in Figure.6.

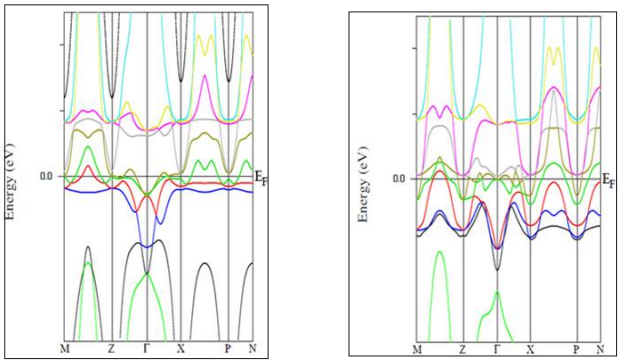

Fig. (6a) Fig. (6b)
Fig. 6. Electronic band structures for T phase (a) and cT phase (b)

In the T-phase, there were several states above the Fermi level which crosses the E_F along the M-Z-X-P direction. This results in a larger density of states at the Fermi level. However for the case of cT-phase, note that most of the bands just above E_F in the T-phase are now just below the E_F in the cT-phas and there is only one band which crosses the E_F along the M-Z-X-P direction. Present result for the T-phase agrees well with previous calculations [21], [22], [23]. The pressure-induced isostructural phase transition to a collapsed tetragonal at ambient temperature is not unique among arsenic compounds that have $ThCr_2Si_2$-type structure. The effect is found among the phosphides that are isostructural to AT_2As_2 compounds such as $EuCo_2P_2$, $SrNi_2P_2$ and $EuFe_2P_2$ [24]. These phosphides compounds have been widely studied and the rapid decrease observed in their *c/a* ratios in the collapsed tetragonal phase has been attributed to bonding transitions associated with the formation of a P–P single bond between ions in adjacent planes along the *c* axis [25].

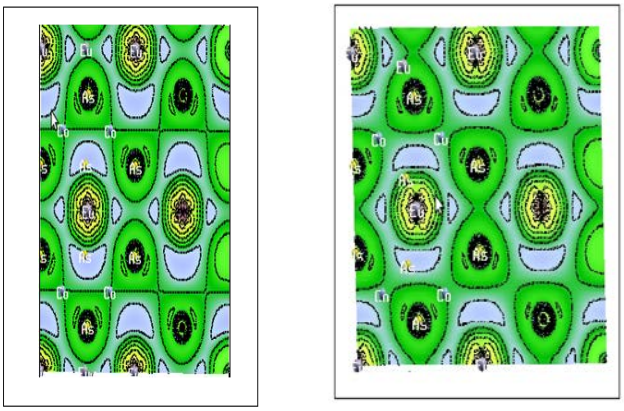

Fig. (7a) Fig. (7b)
Fig. 7. Valance charge density for Tetragonal (a) and cT (b)

In connection to arsenic compounds, recent theoretical calculations for $CaFe_2As_2$ suggest that there is a similar transition in the bonding character of As ions and the enhancement of the As–As bonds across the Fe_2As_2 layers under pressure [11]. In order to reveal that there is large hybridization between As ions in the Eu122 system, show the contour plots of the relevant orbitals in Figure 7. It is clear that the As ion below the top Co-plane makes a bond (or hybridizes) with the arsenic ion which is above the lower Co-plane. Hence this overlap of the As-As along the c-axis makes this system quite isotropic and far from being layered system.According to bond-population analysis, the As-As bond strength increased in the cT-phase. Due to close proximity of the As ions in adjacent Co-layers, the observation of the As-As interaction is natural. It is interesting to note that there is almost the same type of hybridization between two arsenic ions on the same Co-plane as shown in the right panel of collapsed tetragonal phase. The present results are also good agreement with the previous reported 122 type compound of $CaFe_2As_2$ system [11].

6 Conclusion

In the present study structural phase stability, high pressure behavior and electronic structure of $EuCo_2As_2$ was investigated using WIEN2K code. The GGA calculated structural parameter obtained from the present study is in agreement with the experimental values. Present study reveals that this compound undergoes a structural phase transition from Tetragonal phase into Collapsed Tetragonal structure under pressure. The phase transition pressure obtained in this work agrees well with the recent experimental value. The present investigation also indicates that the Tetragonal structure $EuCo_2As_2$ is energetically more stable at ambient conditions. The bonding analysis of collapsed tetragonal phase make known that As-As interactions is strong during the compression along c- axis. The strength of this interaction is mainly controlled by the Co-As chemical bonding.

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References

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, "Iron-based layered superconductor La[$O_{1-x}F_x$]FeAs(X=0.05-0.12) with Tc=26 K," J. Am. Chem. Soc. 130 (2008),3296.

[2] T. Terashima, M. Kimata, H. Satsukawa, A. Harada, K. Hazama, S. Uji, H.S. Suzuki, T. Matsumoto, and K. Murata, "$EuFe_2As_2$ under High Pressure: An Antiferromagnetic Bulk Superconductor," J. Phys. Soc. Jpn. 78(2009), 083701.

[3] W. Uhoya, G. Tsoi, Y.K. Vohra, M.A. McGuire, A.S. Sefat, B.C. Sales, D. Mandrus and S.T. Weir, "Anomalous Compressibility effects and superconductivity of $EuFe_2As_2$ under high pressures," *J. Phys.: Condens.Matter* 22 (2010)292202.

[4] R. Mittal, S.K. Mishra, S.L. Chaplot, S.V. Ovsyannikov, E. Greenberg, D.M. Trots, L. Dubronvinsky, Y. Su, T. Brueckel, S. Matsuishi, H. Hosono and G. Garbarino, "Ambient- and low-temperature synchro-

tron x-ray diffraction study of $BaFe_2As_2$ and $CaFe_2As_2$ at high pressures up to 56 GPa," *Phys. Rev.* B 83(2011), 054503.

[5] W. Uhoya, A. Stemshorn, G. Tsoi, Y.K. Vohra, A.S. Sefat, B.C. Sales, K.M. Hope and S.T. Weir, "Collapsed tetragonal phase and superconductivity of BaFe2As2 under high pressure," *Phys. Rev.* B 82(2010), 144118.

[6] C. Huhnt, W. Schlabitz, A. Wurth, A. Mewis and M. Reehuis, "First order phase transitions in $EuCo_2P_2$ and $SrNi_2P_2$," *Phys. Rev.* B 56(1997), 13796.

[7] C. Huhnt, W. Schlabitz, A. Wurth, A. Mewis and M. Reehuis, "First- and Second-order phase transition With $ThCr_2Si_2$-type structure," *Physica* B 252 (1998),44.

[8] Ruben Gatt and Joseph N. Grima, 'Negative Compressibility,' Phys.stat.sol. (RRL) 2, No.5, 236-238 (2008).

[9] S. Torikachvilli, S.L.Bud'Ko, N. Ni, P.C. Canfield, "Pressure induced superconductivity in $CaFe_2As_2$," Phys.Rev.Lett 101(2008), 057006.

[10] W.Yu, A.A .Aczel, T.J. Williams, S.L.Bud'Ko, N. Ni, canfield P C and Luke G M "Absence of superconductivity in single phase $CaFe_2As_2$ under hydrostatic pressure," Phys.Rev.B.79 (2009),020511 (R).

[11] T.Yildirium, "Giant Coupling of Fe-spin and the As-As Hybridization in Iron-Pnictides," Phys.Rev.Lett 102(2009), 037003.

[12] Micheal Widom, Khandlker Quader, "First Principles Study of $CaFe_2As_2$ Collapse under Pressure," arXiv: 1207.4550v1 [Cond-Mat-Str-el] 19 Jul (2012).

[13] Jared Ballinger, Lowell E. Wenger, Yogesh K. Vohra, and Athena S. Sefat, "Magnetic properties of single crystal $EuCo_2As_2$," Journal of applied physics 111(2012), 07E106.

[14] Matthew Bishop, Walter Uhoya, Georgiy Tsoi, Yogesh K Vohra, Athena S Sefat andBrianC Sales, "Formation of collapsed tetragonal phase in $EuCo_2As_2$ under high pressure," J.Phys.: Condens. Matter 22 (2010) 425701 (5pp).

[15] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka and J. Luitz 2001 WIEN2k, "An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties," (Wien, Austria: Karlheinz Schwarz, Tech. Universitat Wien).

[16] J.P. Perdew, K. Burke and M. Ernzerhof, "Generalized approximation made simple," Phys. Rev. Lett. 7(1996), 3865.

[17] F. Birch, "Finite strain isotherm and velocities for single-crystal and polycrystalline NaCl at high pressures and 300°K," J. Geo. Phys. Rev. 83 (1978),1257.

[18] Venkatachalam Jayalakshmi, Ramaswamy Murugan, Balan Palanivel, "Electronic and structural properties of $CuMO_2$ (M = Al, Ga, In)," Journal of Alloys and Compounds 388(2005), 19-22.

[19] N. E. Christensen, A. Svane, R. Laskowski, B. Palanivel,P. Modak, A. N. Chantis, M. van Schilfgaarde, andT. Kotani, "Electronic properties of 3*R*-CuAlO2 under pressure: Three theoretical approaches," *Phys. Rev.* B 81(2010), 045203.

[20] M. Born, K. Huang, "Dynamical Theory of Crystal Lattices," Clarendon, Oxford, 1954.

[21] I. I. Mazin, "Problems with reconciling density functional theory calculations with experiment in ferropnictides," Phys. Rev. B 78(2008), 085104.

[22] V. Vildosola, "Bandwidth and Fermi surface of iron oxypnictides: Covalency and sensitivity to structural changes," Phys. Rev B 78(2008), 064518.

[23] D. J. Singh, "Electronic structure and doping in $BaFe_2As_2$ and LiFeAs: Density functional calculations," Phys. Rev. B 78(2008), 094511.

[24] B. Ni, N.M. Abd-Elmeguid, H. Micklitz, J.P. Sanchez, P.Vulliet and D. Johrendt, "Interplay between structural, Electronic, and Magnetic instabilities in EuT_2P_2(T=Fe,Co) under high pressure," *Phys. Rev.* B 63 (2001)100102(R).

[25] R. Hoffmann and Zheng, "Making and Breaking Bonds in the Solid State: The $ThCr_2Si_2$ Structure," *J. Phys. Chem.* 89 C (1985) 4175.