Journal of Alloys and Compounds 522 (2012) 106–113

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

A first principles calculations of structural, electronic, magnetic and dynamical properties of mononitrides FeN and CoN

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ARTICLE INFO

Article history:
Received 28 November 2011
Received in revised form 11 January 2012
Accepted 16 January 2012
Available online 28 January 2012

Keywords:
First principles
Spin
Phonon
Bandstructure

ABSTRACT

Using first principles density functional theoretical calculations, the present paper reports a systematic nonspin and spin polarized total energy calculations of the lattice dynamical and a number of other properties such as band structure, structural and magnetic moment of two mononitrides FeN and CoN. The phonon dispersion curves and phonon density of states in the case of FeN and CoN have been determined for the first time and discussed. The structural and dynamical calculations suggest that the zinc blende structure is preferred at ambient pressure for both compounds. The rocksalt FeN has a nonzero magnetic moment while for FeN in zinc blende phase, it is either zero or very small. The zinc blende phase for both compounds is nonmagnetic. The spin calculation offers an intensive opportunity to understand the role of spin on the phonon properties of two mononitrides. Majority of the modes are sensitive to the effect of spin due to the modification of lattice constant. In this work we reveal that spin modifies the interionic interactions and local structure and leads to a flexible lattice which can be used for the functional materials design.

1. Introduction

In recent past the transition metal mononitrides have attracted a lot of research interests as they are known to be refractory compounds characterized by high hardness, brightness, high melting point and high temperature resistance [1], which make them attractive in many applications. Some of these compounds also have interesting magnetic properties [2,3]. The iron rich iron nitride (FeN) is an important material to be useful pigments for high magnetic density [4], while high N-content FeN is considered to be an interesting material in spintronics.

Most of the early transition metal nitrides crystallize in rock salt (RS) structure; however the structure in ground state for FeN and CoN is still an important issue as both rock-salt (RS) and zinc blende (ZB) structures have been reported for these compounds in the literature [4–17]. Recently, two different structures for FeN and CoN have been suggested [5–9]. Using hyperfine splitting from Mössbaur spectroscopy, it was suggested that the FeN in zinc blende and rocksalt phases shows nonmagnetic and antiferromagnetic (AFM) coupling respectively [5–9]. Suzuki et al. [6] found that the zinc blende FeN is AFM and exhibits a micromagnetic character due to instability resulting from zero energy difference between magnetic and nonmagnetic states of two structures. In the case of CoN, two separate synthesis resulted into two different structures; zinc blende [9] and rocksalt [10], surprisingly with almost same lattice constant of about 4.28 Å.

Numerous theoretical investigations [9–13], of FeN and CoN have been performed during past few years using the first principles density functional theoretical calculation to get insight of their physical properties and to discuss the experimental discrepancy. These studies include electronic structure, magnetism and phase stability of these compounds. A clear controversy exists between the studies carried out so far using first principles method. Shimizu et al. [10] have showed ferromagnetic RS FeN to be more favourable than nonmagnetic ZB FeN. Filippetti and Pickett [15] and Kong [11] from two independent studies later found that the FeN is stable in rock salt phase but there was disagreement for the magnetic ordering. Eck et al. [16] and Lukashev and Lambrecht [12] predicted a stable nonmagnetic ZB-FeN. In a recent study, Houari et al. [13] found that the ferromagnetic RS phase is more stable than the ZB and wurtzite (w) type structures for FeN. In the case of CoN, Suzuki et al. [17] suggested this compound to be paramagnetic, while Lukashev and Lambrecht [12] reported zero magnetic moment for ZB-CoN. Under pressure, these compounds transform from ZB to RS phase at 30 ± 5 and 50 ± 10 GPa for CoN and FeN respectively [12], which needs to be verified from other calculations due to a large error bar along with the clarification on ground state phase.

To our knowledge, the phonon properties and role of spin–lattice interaction, which are the important properties for solids showing magnetism, have not been attempted either

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doi:10.1016/j.jallcom.2012.01.100

theoretically or experimentally until now for any of these compounds. The influence of magnetism to phonon has been investigated by Kim [18] in the framework of mean field theory about 30 years ago and found that the spin–lattice interaction may have significant effects in the magnetization depending on the density of states near the Fermi level. It is found from the local density approximation (LDA) calculation that the spin–phonon interactions are negligible in the stable phase (bcc) of Fe [19]. However, the fcc phase develops soft magnons leading to a stronger spin–phonon interaction. This results into the less unstable lattice against spin (magnon) excitations. Consequently, the main purpose of this work is to provide some additional information to the existing data on the structure, magnetic ordering and phase transition in FeN and CoN using the nonspin and spin polarized ab initio total energy calculations. The aim of the present work is to perform a systematic study on the structural, electronic, magnetic and phonon properties of two mononitrides FeN and CoN. We also aim to analyze the spin–lattice interaction in these compounds. It is noteworthy to mention that the phonon calculations and spin–lattice interaction analysis for any nitride is being performed for the first time using ab initio calculation.

A brief description of the computational method will be presented in next section. In Section 3, we present the calculated results and discuss them in the light of available data. A short summary is presented in Section 4.

2. Methodology

We have used the plane wave self consistent field implementation of density functional theory (DFT) with generalized gradient approximation (GGA) [20] implemented in Quantum ESPRESSO [21]. The exchange correlation energy and ultrasoft pseudopotentials are used to represent the interaction between ionic cores and valence electrons. The electronic wave functions are represented in plane wave basis set with a kinetic energy cut off 98 (90) Ry for both phases of FeN (CoN). The self consistent calculations are considered to be converged when the total energy of the system is stable within convergence of $E_{\mathrm{tot}} < 2.73 \times 10^{-3}$ eV. The Brillouin zone (BZ) investigations are carried out by the Gaussian smearing technique using a 4 × 4 × 6 and 8 × 8 × 8 point mesh with shift from origin for FeN and CoN respectively. The number of sampling **k**-points used in the Brillouin zone (BZ) summation of the electronic density and total energy is increased until the total energy converges to the desirable tolerance. Thirty-six special **k**-points in the irreducible BZ are sufficient to achieve the convergence for the total energy. To generate the **k**-point mesh in the BZ, the scheme of Monkhorst–Pack [22] has been used.

The phonon dispersion curves are calculated within density functional perturbation theory (DFPT) [23]. In this method, the dynamical matrix which provides information on lattice dynamics of the system is obtained from the ground state electron charge of the nuclear geometry. The kinetic energy cut off and numbers of **k**-points mentioned above are found to yield phonon frequencies converged to within 2–5 cm^{-1}. The dynamical matrices are calculated on a 4 × 4 × 4 grid.

3. Results and discussion

There exist few investigations on structural and magnetic properties for FeN and CoN; however care needs to be exercised in commenting on the success of calculations based on the validation of several properties.

Fig. 1 presents the energy versus lattice constant for FeN and CoN in zinc blende and rocksalt phases, which reveals that the lower energy minimum occurs for ZB phase and at larger lattice constant than for rocksalt phase in both compounds. The lattice constant, bulk modulus and its pressure derivative for FeN and CoN in both phases are obtained fitting to the equation of state to Murnaghan analytical expression of 3rd order [24] and presented in Table 1 along with the experimental and other theoretical results. The calculated lattice constant and bulk modulus values obtained for FeN and CoN in ZB and RS phases agree better to the experiment than the previously reported theoretical values. Now turning to the spin polarized calculations, Table 1 presents the nonspin and spin polarized results separately in groups and the under binding effect of spins can be clearly seen. Furthermore, it is seen from the total energy versus lattice constant plots for nonspin and spin polarized cases for both compounds that there is not a significant effect of spin for ZB-FeN as well as both phases of CoN. This is also supported from the magnetic moment values listed in Table 1. We find from Table 1 that there is no magnetic moment in the CoN for either phase, while for ZB-FeN it is quite low 0.04 μ_B. The magnetic moment of 2.41 for RS-FeN is in good agreement with previously reported magnetic moment value at its equilibrium lattice constant [8,13]. It is further observed from Fig. 1 that the nonmagnetic state of FeN in the RS phase is favoured at the calculated equilibrium lattice constant similar to the one reported in Refs. [12,13]. There is a zero difference in energy between magnetic and nonmagnetic states which is in agreement with previous work [13]. However, for larger volumes they diverges the present estimated theoretical lattice constant in spin polarized case for the ZB phase of FeN and CoN agrees quite well with the experimental data. There is a significant difference between theoretical and structural lattice constant values in the case of RS phase of both compounds similar to previous reports. However, the present values are closure to experiment than previous reported values [12,13]. A common explanation for this difference is attributed to the two effects: firstly to the surface effects as the samples are thin films and secondly to the non-stoichiometry of the elaborated samples [13].

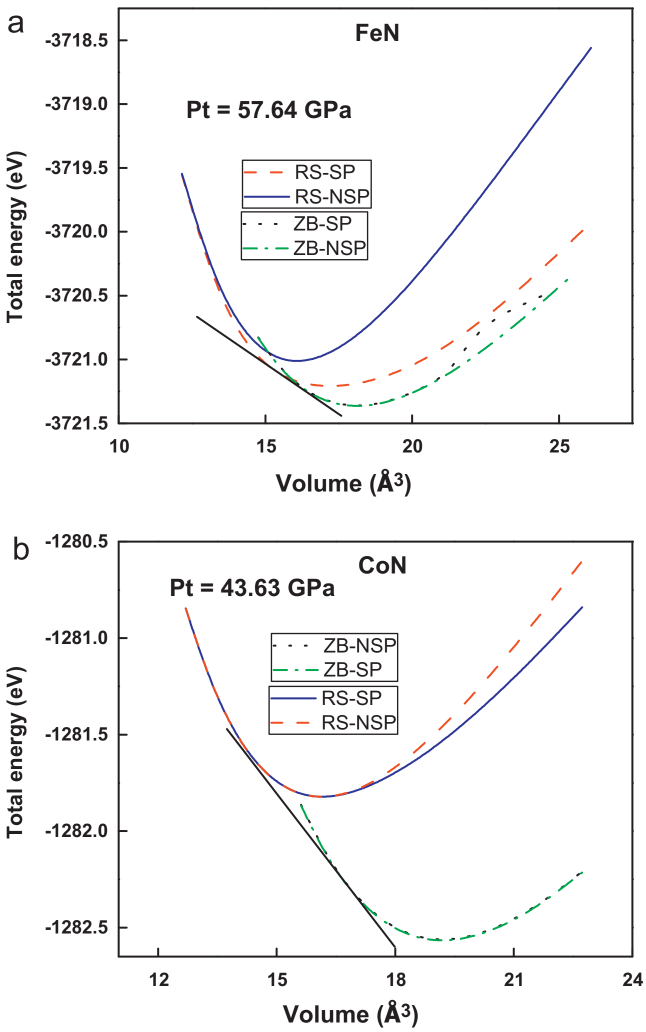

Fig. 1. Total energy per atom (in eV) vs. volume per atom (in Å^3) for FeN and CoN in the rock salt and zinc blende structures in spin polarized and nonspin polarized cases where the slope of tangent line is 57.64 and 43.63 for FeN and CoN NSP case respectively.

Table 1
Calculated equilibrium lattice constants, magnetic moment, bulk modulus and first order pressure derivative of bulk modulus for FeN and CoN in RS and ZB phases for both nonspin polarized and spin polarized cases.

Compound		*a* (Å)	Magnetic moment (μ_B)	*B* (GPa)	*B*′
FeN RS	Experiment (NSP)	4.5709,[h] 4.355[i]			
	Present	3.9966		318	1.0
	Other	3.9369 (ASA-LDA)[b]		395,[b] 370[b]	4.5,[b] 4.5[b]
		3.9670 (ASA-GGA)[b]		369[b]	4.6[b]
		3.9799 (FP-LDA)[b]			
		4.0239[e]			
	(SP) Present	4.1041	2.41	186	4.77
		3.9599 (ASA-LDA)[b]	2.62,[c] 2.60[e]	316,[b] 248[b]	5.6,[b] 5.8[b]
		4.0209 (ASA-GGA)[b]			
	Other	4.0149 (FP-LDA)[b]	2.36[e]	288[b]	5.2[b]
		4.1100,[e] 3.9989,[f]			
		4.1999[g]			
FeN ZB	Experiment (NSP)	4.307,[a] 4.524[i]			
	Present	4.232		265	4.42
	Other	4.1689 (ASA-LDA)[b]		322,[b] 308[b]	
		4.1950 (ASA-GGA)[b]		324[b]	
		4.2148 (FP-LDA)[b]			
		4.3380[e]			
	(SP) Present	4.2250	0.04	266	6.65
	Other	3.9599 (ASA-LDA)[b]	0.00[c]		
		4.0209 (ASA-GGA)[b]			
		4.0149 (FP-LDA)[b]			
		4.3480,[e] 4.3590,[f]			
		4.1969[b]			
CoN RS	Experiment (NSP)	4.2969[d]			
	Present	4.0104		269	4.88
	Other	3.9315 (ASA-LDA)[b]		378,[b] 350[b]	4.6,[b] 4.7[b]
		3.9639 (ASA-GGA)[b]		352[b]	4.6[b]
		3.9717 (FP-LDA)[b]			
	(SP) Present	4.0103		235	5.61
	Other				
CoN ZB	Experiment (NSP)	4.297[d]			
	(NSP) Present	4.2511		233	4.22
	Other	4.1819 (ASA-LDA)[b]		302,[b] 283[b]	4.4,[b] 4.4[b]
		4.2149 (ASA-GGA)[b]		294[b]	4.9[b]
	(SP) Present	4.2759 (FP-LDA)[b]		233	4.22
	Other	4.2512			

[a] Ref. [6].
[b] Ref. [12].
[c] Ref. [8]
[d] Ref. [17].
[e] Ref. [13].
[f] Ref. [10].
[g] Ref. [11].
[h] Ref. [5].
[i] Ref. [7].

Turning now our attention to the bulk modulus; we can see from Table 1 that bulk modulus for both compounds are in the range of other calculated values. The slight low values of bulk modulus can be attributed to the GGA as it is known that the GGA underestimates the bulk modulus as the cohesive energy is underestimated in the case of GGA.

The occurring of energy minimum at relatively larger lattice constant than equilibrium lattice constant in the case of zero pressure phase (Fig. 1) may lead to phase transition at higher pressure from preferred zero pressure phase. We determine the phase transition pressure using the common tangent method as shown in Fig. 1(a) and (b) for FeN and CoN respectively. The phase transition pressure, obtained so is 57.6 GPa and 43.6 GPa for FeN and CoN respectively agree reasonably well with the previous study [12] (FeN at 50 ± 10 GPa and CoN at 30 ± 5 GPa). The phase transition occurs from zinc blende (zero pressure) to rocksalt phase in the case of both mononitrides. It is noteworthy that for ZB-FeN the magnetic line (spin calculation) begins to approach nonmagnetic line very closely and finally they merged by making a hump. This may be attributed to a magnetic phase transition from magnetic to nonmagnetic state.

The electronic band structure along with the density of states for both nonspin and spin cases in ZB and RS phases of FeN and CoN are plotted in Figs. 2 and 3 respectively. The nonspin polarized density of states reflects all usual features of bandstructure. The DOS shows that the Fermi level lies on a strong peak in the case of FeN-RS while the same is in gap for FeN-ZB. This is quite similar to the DOS obtained in Ref. [12]. The resolved density of states (DOS) is plotted in Figs. 4 and 5 respectively for FeN and CoN. The Fermi level is set to be zero. In case of FeN the DOS is resolved in N 2p and Fe 3d states in both RS and ZB phases (Fig. 4), while in the case of CoN, DOS is resolved in N 2p and Co 1s states for both RS and ZB phases (Fig. 5). It is clear from the band structure and DOS of RS-FeN that there is a stronger hybridization of N and Fe bands with several bonds crossing the Fermi level. The stronger hybridization of bands and crossing of Fermi level by bands are also observed for both phases of CoN. These are similar to the previous band structure reports on FeN and CoN and indicate that the Fermi sphere may be complex [12]. To confirm this we analyzed the Fermi sphere (FS) and charge contour (not shown) for both compounds. A common feature observed in the FS plot is that the charge carriers are predominately hole like. In addition, a tendency to nesting instabilities of the Fermi surface

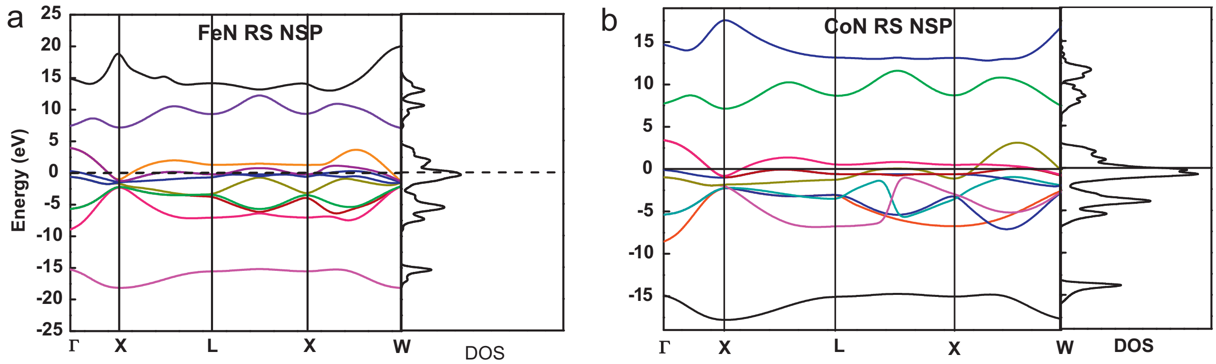

Fig. 2. The electronic band structure and corresponding density of states for FeN and CoN using the GGA pseudopotential for RS phase. The Fermi energy is set to be zero as shown by dashed horizontal line.

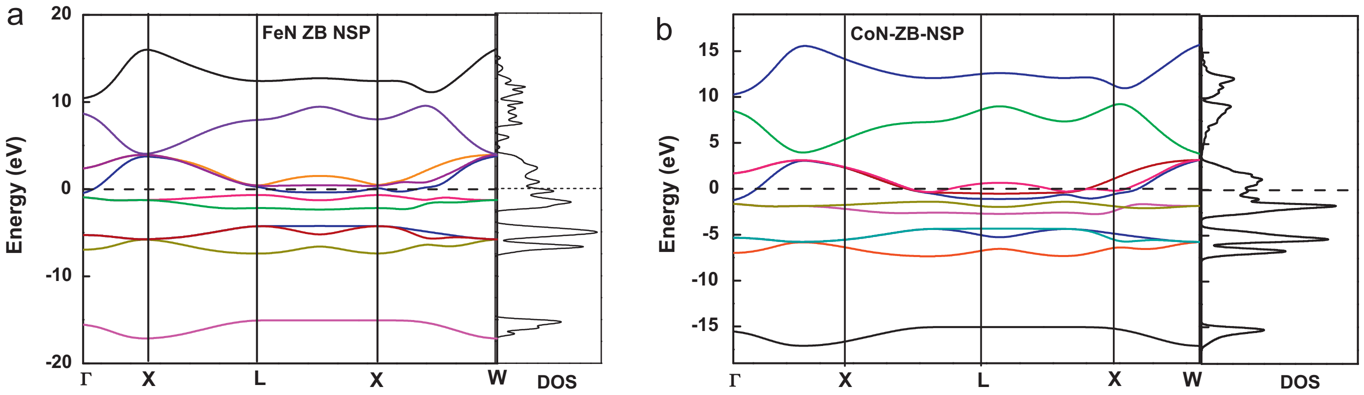

Fig. 3. The electronic band structure and corresponding density of states for FeN and CoN using the GGA pseudopotential for ZB phase. The Fermi energy is set to be zero as shown by dashed horizontal line.

sheets is observed. Furthermore, from the significant proportion of the Fermi surface a somewhat large number of carriers are expected and thus a metallic behaviour can be inferred for these compounds, which is clearly visible in the DOS. Now turning our attention to the density of states particularly in the light of stability of the structure, bonding and magnetism are due to the implementation of spin in the calculations. In addition, the Stoner criterion is only satisfied for FeN-RS similar to earlier studies [5,6,10–13].

Figs. 6 and 7 present the variation of magnetic moment as a function of lattice constant for FeN and CoN respectively. It is seen from Fig. 6 that the variation of magnetic moment in the case of FeN shows a sudden change at 4.4965 Å for ZB and nonlinear variation for RS phase similar to the one reported in Refs. [12,13]. The variation is nonlinear with a rapid change slightly above the equilibrium lattice constant for RS. For, CoN we do not get any magnetic moment at equilibrium lattice constant in either phase. This indicates that the CoN is a nonmagnetic compound similar to the experimental observation [17] and earlier theoretical study [12]. However, at higher lattice constant value in both ZB and RS phases the nonmagnetic compound CoN acquires a magnetic moment. The variation of magnetic moment with lattice constant shows similar behaviour as observed in the case of FeN. It is important to note that the higher magnetic moment in both compounds can be achieved for both phases at volume more than the equilibrium volume. The higher

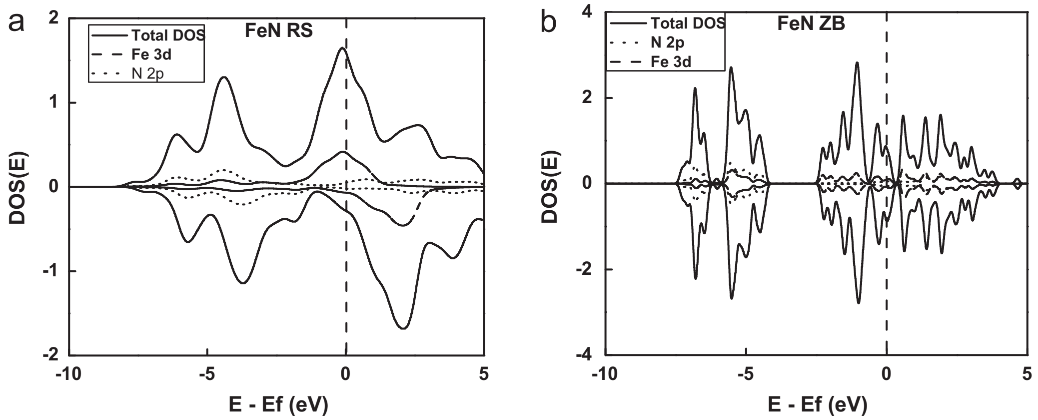

Fig. 4. Spin polarized electronic density of states for FeN in both RS and ZB phases.

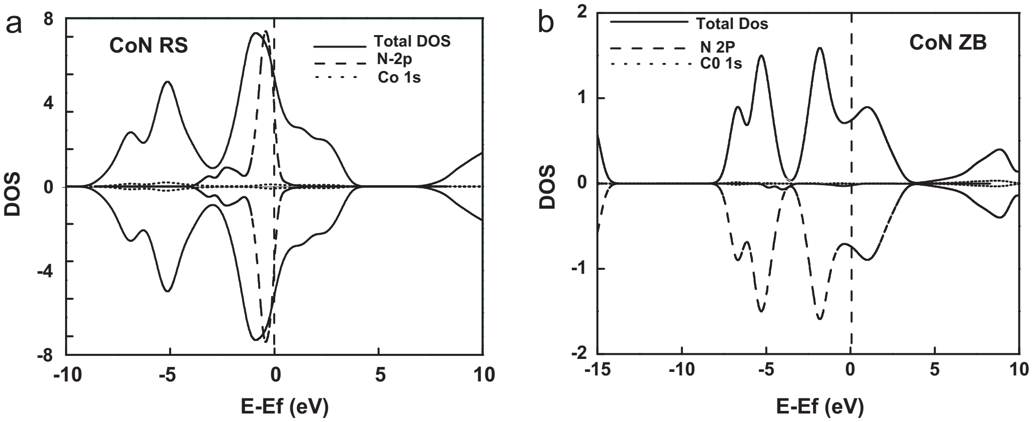

Fig. 5. Spin polarized electronic density of states for CoN in both RS and ZB phases.

magnetic moments at larger lattice constants than its equilibrium lattice constant indicate a atom like behaviour [12].

Energy dispersion of phonons provides important information about the dynamical properties of materials. In particular, it is essential in the calculation of specific heat, sound velocity, thermal expansion, heat conduction, vibrational entropy, free energy via quasiharmonic approximation, electron–phonon interaction etc. Furthermore, low frequency modes can be associated with phase transformations, while imaginary frequencies show that the structure is dynamically unstable. It is important to note that the phonon properties for FeN and CoN are investigated for the first time and hence could not be compared with any experimental data and the results are predictive only. Figs. 8 and 9 present the phonon dispersion curves for FeN and CoN in zinc blende phase. It is clearly seen from these figures that the FeN and CoN are dynamically stable in the ZB phase as the phonons are positive throughout the Brillouin zone. Fig. 10 shows the phonon dispersion curves for FeN and CoN in RS phase contains imaginary frequencies for phonon modes. This indicates instability in the structure. The stabilized phonon modes in Figs. 8 and 9 are divided into two parts: the lower band ranging up to 300 cm^{-1} (250 cm^{-1}) is mostly attributed due to Fe (Co) atom vibrations while higher band is formed by N atom vibrations. It is seen from these figures that there is a clear gap (more in the case of FeN) between the optical and acoustical branches for both compounds due to large mass ratio of constituent atoms. The degenerate LO and TO phonon modes for both compounds are quite dispersive in the *Γ*–*X* direction of the Brillouin zone. The degenerate optical modes at zone centre confirm their metallic character as observed from electronic band structure and DOS. It is however important to note that there will be a significant stronger Drude

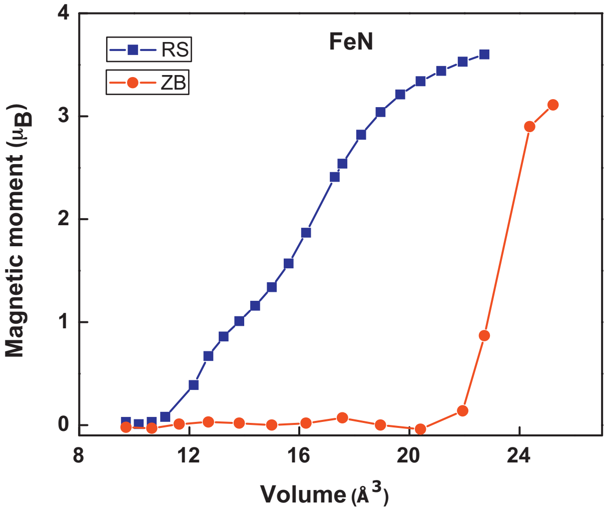

Fig. 6. Variation of magnetic moment as a function of lattice constant for FeN.

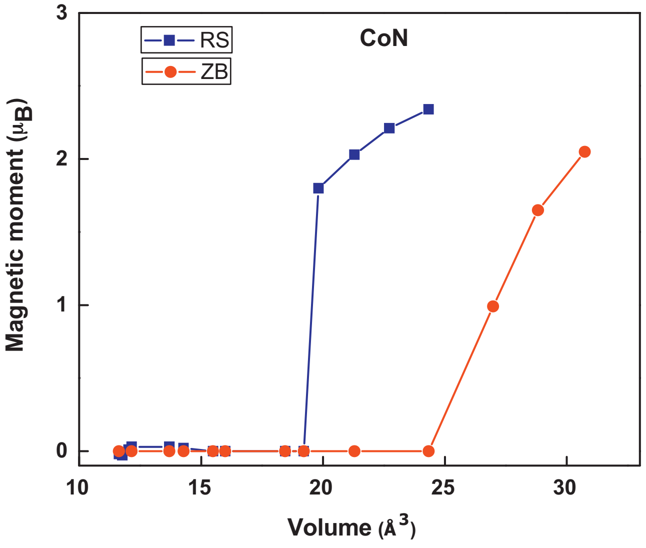

Fig. 7. Variation of magnetic moment as a function of lattice constant for CoN.

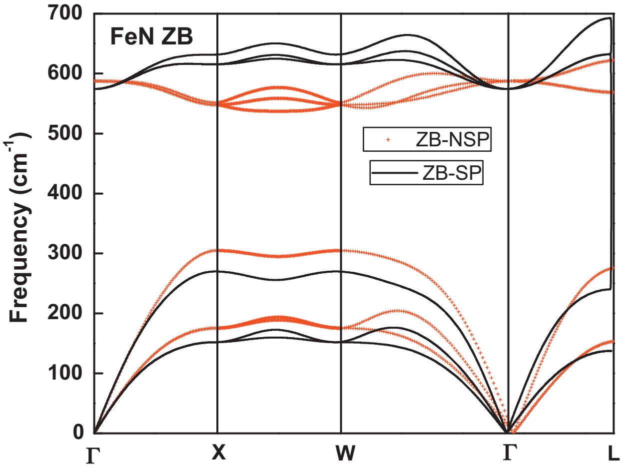

Fig. 8. The phonon dispersion curves of FeN ZB phase for spin polarized and nonspin polarized.

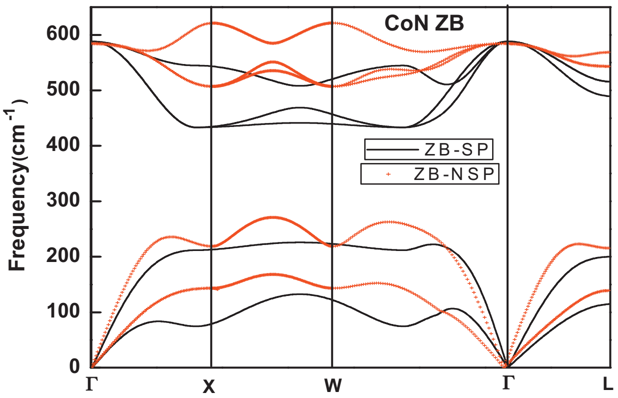

Fig. 9. The phonon dispersion curves of CoN ZB phase for spin polarized and nonspin polarized.

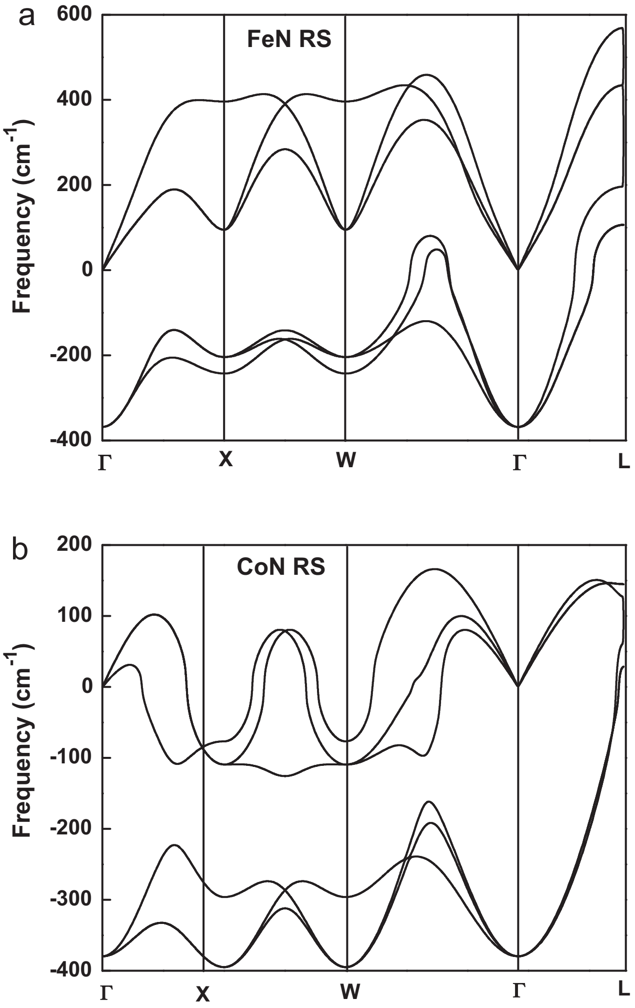

Fig. 10. The phonon dispersion curves for RS phase of FeN (a) and CoN (b).

Table 2
Calculated zone cantered phonon frequency at Gamma of Brillouin zone for FeN and CoN for both non polarized and spin polarized cases.

Compound	Zone centre frequencies (cm^{-1})	
	NSP	SP
FeN ZB	586.7	591.8
CoN ZB	584.7	587.7

free carrier absorption in these materials due to high metallic carrier density. This will lead to the stronger LO–plasmon coupling as observed in the case of ScN [25]. Travaglini et al. [25] have analyzed the decoupled phonon and carrier contributions from plasmon in the far-infrared region using two band model and observed that the most of the change is intrinsic suggesting ScN to be semi metallic. The transverse acoustical (TA) branch is slightly softer in the case of CoN which shows that the phase transition in the case of CoN may be driven by TA phonons.

To determine the effect of spin on various phonons, we have calculated the phonon dispersion curves for both compounds in its optimized zinc blende phase with the effect of spin. It is important to note that the magnetic moment is zero for these compounds in ZB phase. However, an additional energy due to spin is added to the total energy and expansion of lattice is expected. The electronic states are greatly modified from the localized moment, which may increase the lattice constant while net magnetic moment cancel out each other. The spin polarized calculations of phonon dispersion curves for both compounds in ZB phase are presented in Figs. 8 and 9 along with the phonon dispersion curves calculated without spin. We observe that the phonon frequencies are sensitive to the spin. These figures depict that the optical branches become strongly dispersive with modified frequencies, clearly seen at the symmetry points with inclusion of spin. In the case of acoustic phonons, a closure inspection of the dispersion curves reveals subtle modification. It is noteworthy that the acoustic phonons show different trend in both compounds after including the spin effect. While there is an increase in the frequency of acoustic phonon throughout the Brillouin zone (BZ) for CoN, the frequency decreases for acoustic phonons in the case of FeN. In the case of optical phonons for both compounds have similar trend i.e. the frequency increases after the inclusion of spin. These may be due to the fact that the magnetic phase favours smaller volume which increases the force. However, there is no change in the nature of the dispersion. The frequency of optical modes at zone centre is almost unaltered. There is a remarkable feature in the phonon dispersion curves of ZB-CoN with the inclusion of spin. A kink near X point and towards Γ–W line in case of TA branch disappears. A softening is observed at X and W points of Brillouin zone in the case of LA phonons. It is however, important to note that the energy vs. volume curves for nonmagnetic and magnetic cases overlap. Table 2 compares the zone centre frequencies for both nonspin and spin polarized cases. We observe that there is a change in the infrared active optical phonon (phonons are triply degenerated and there is no LO–TO splitting at zone centre). The phonon frequency for infrared phonon modes increases in the case of spin calculations for both FeN and CoN. The increase is however more prominent in the case of FeN than CoN.

The general condition for stable structure in terms of lattice dynamics is that all phonon modes have real frequencies. A negative value of frequency of any of these modes leads system to dynamical instability. To check this, one has to consider the stability against three distinct types of deformation; long wavelength homogeneous deformations related to zone centre acoustic modes, long wavelength inhomogeneous deformations related to all other zone boundary modes [26]. A decrease in frequency of any of these modes means that the system is approaching the limit of dynamical instability. Fig. 11(a) and (b) presents the pressure variation of TA phonon mode of FeN and CoN in ZB phase at X-point of Brillouin zone. It is clearly seen from figure that the application of pressure above 57 GPa and 91 GPa respectively for FeN and CoN results into the negative phonon frequencies indicating the dynamical instability of ZB. This indicates that the phase transition in the mononitrides from ZB to RS is driven by transverse acoustic phonon mode. However, it is observed that the phonon instability is taking

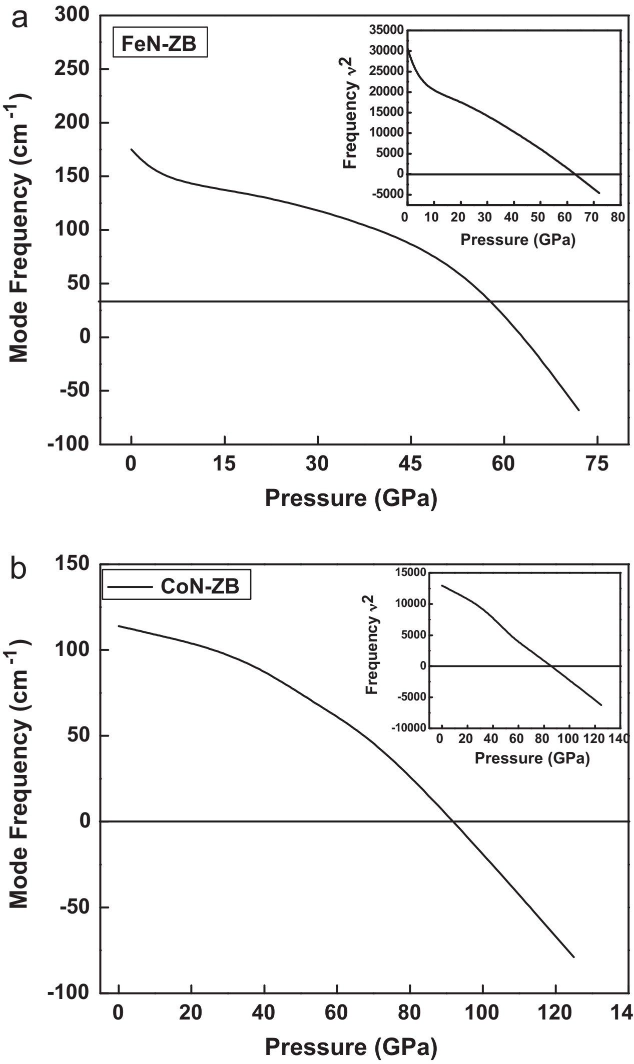

Fig. 11. Pressure dependence of the TA phonon frequency of ZB structure of FeN (a) and CoN (b).

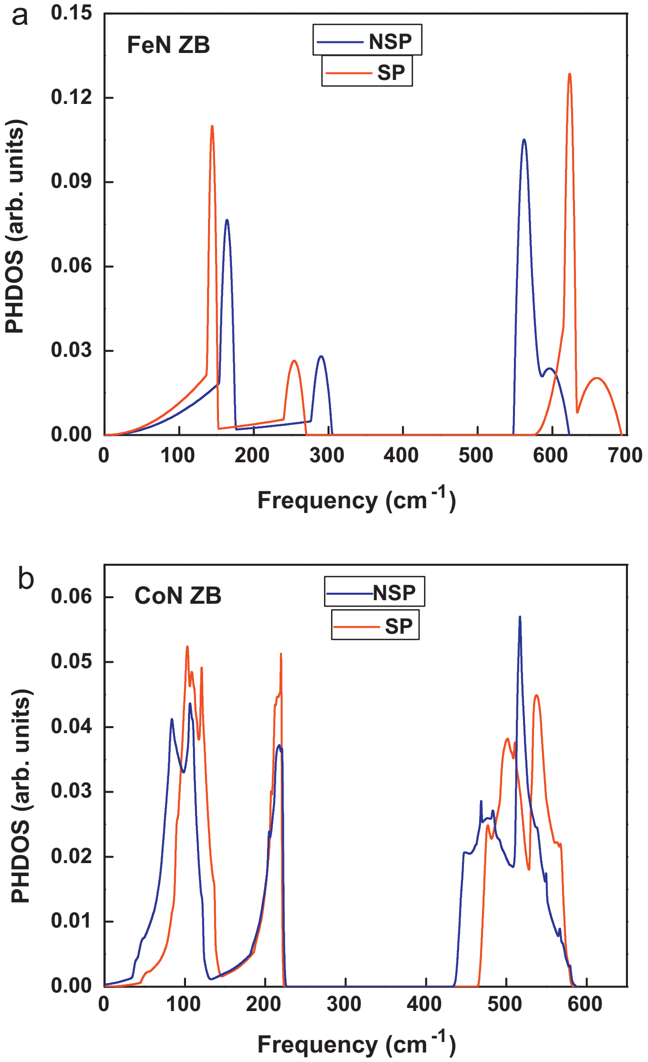

Fig. 12. Calculated phonon density of states for nonspin polarized and spin polarized FeN and CoN.

place at a pressure higher than that predicted from total energy calculation in the case of CoN.

In Fig. 12, we present the phonon density of states of ZB-FeN and ZB-CoN for both nonspin and spin polarized calculations to see the effect of spin on the phonon spectrum. While the shapes of the spectra are very similar, they differ with respect to the frequency scale. This is consistent with the observation in the case of double perovskite in which the frequencies of infrared active phonons shift due to the inclusion of spin [27]. There is a gradual shift of peaks to the higher side (red shift) in the higher wave number, while the lower wave number peaks are blue shifted after inclusion of spin in the case of FeN. However, the prominent modifications are mostly observed in middle regions. It is noteworthy that there is no effect of spin on the peak at 200 cm^{-1} peak for CoN. However, it is clear from figure and Table 2 that the majority of vibrational modes are sensitive to the spin. The observed changes in the phonon spectra after inclusion of spin might have an underlying electronic origin as there is no change in lattice parameter with the inclusion of spin particularly for CoN. We find that behaviour of the electronic density of states at the Fermi level is different. This may be due to the fact that the magnetic moment is determined from the contributions of electrons and phonons to the free energy [18]. This may further be attributed to the large DOS at Fermi level in the case of FeN. Therefore, it confirms that the spin modifies interionic interactions and local structure and hence the spin in these compounds has important consequences for the design of materials, where many exotic properties derive from a flexible lattice rather than the rigid lattice.

4. Conclusion

A systematic study of the total energy calculations on the lattice dynamics, structure and electronic properties has been performed using pseudo-potential plane wave and generalized gradient approximation for two mononitrides FeN and CoN. We have revealed that the zinc blende phase is in the ground state and the band structure of this phase is metallic in nature for both nitrides. The transition pressure for the zinc blende to rock salt phase is observed about 57.6 GPa and 43.6 GPa for FeN and CoN respectively. Spin polarized calculations suggest that the FeN has a magnetic moment in rocksalt phase. The magnetic moment increases abruptly near a certain critical lattice constant for both materials. Besides we have discussed the dynamical behaviour of FeN and CoN for both phases. The dynamical behaviour of ZB-FeN and ZB-CoN with pressure shows that these compounds are dynamically stable. We predicted a pressure induced soft phonon mode and the zone boundary *X*-point. Dynamical calculations predict the ZB–RS transition to occur at 57 GPa and 91 GPa for FeN and CoN respectively. In the absence of any experimental data on phonons, we think that the ab initio theoretical estimation is the only reasonable tool for obtaining such important information. The spin calculation indicates that the majority of vibrational modes are sensitive to spin inclusion though the magnetic moment is zero. The spin inclusion results in the modification of total energy of the system and hence lattice is expanded. This results into the modification of phonon dispersion curves. The effect is more prominent in FeN than CoN. This is the consequence of spin which modifies the interionic interactions and local structure. The phonon properties and local structure which have important consequence for the design of functional materials.

Acknowledgements

The financial assistance from the Department of Science and Technology and Department of Atomic Energy BRNS, Govt. of India is highly acknowledged. Computations were carried out on the computer cluster PAWAN at the Department of Physics, Bhavnagar University financed by the Department of Science and Technology, Govt. of India and the Department of Atomic Energy, Mumbai.

References

[1] A. Neekel, Int. J. Quantum Chem. 23 (1983) 1317.
[2] A. Leineweber, R. Niewa, H. Jacobs, W. Koekelmann, J. Mater. Chem. 10 (2000) 2827.
[3] L.M. Corliss, N. Elliott, J.M. Hastings, Phys. Rev. 117 (1960) 929.
[4] (a) S.F. Matar, G. Demazeau, B. Siberchicot, IEEE Trans. Magn. 26 (1990) 60;
(b) S.F. Matar, J. Alloys Compd. 345 (2002) 72;
(c) P. Mohn, S.F. Matar, J. Magn. Mater. 191 (1999) 234, and the reference listed therein.
[5] H. Nakagawa, S. Nasu, H. Fujii, M. Takahashi, F. Kanamaru, Hyperfine Interact. 69 (1991) 455.
[6] K. Suzuki, H. Morita, T. Kaneko, H. Yoshida, H. Fujimori, J. Alloys Compd. 201 (1993) 11.
[7] L. Rissanen, M. Neubauer, K.P. Lieb, P. Schaaf, J. Alloys Compd. 274 (1998) 74.
[8] T. Hinomura, S. Nasu, Hyperfine Interact. 111 (1998) 221.
[9] O. Schmidt-Dumont, N. Kron, Angew. Chem. 67 (1955) 231.
[10] H. Shimizu, M. Shirai, N. Zuzuki, J. Phys. Soc. Jpn. 67 (1998) 922.
[11] Y. Kong, J. Phys. Condens.: Matter 12 (2000) 4161.
[12] P. Lukashev, W.R.L. Lambrecht, Phys. Rev. B 70 (2004) 245205.
[13] A. Houari, S.F. Matar, M.A. Belkhir, M. Nakhl, Phys. Rev. B 75 (2007) 064420.
[14] B. Taylor, B. Joyner, F.H. Verhoek, J. Am. Chem. Soc. 83 (1961) 1069.
[15] A. Filippetti, W.E. Pickett, Phys. Rev. B 59 (1999) 8397.
[16] B. Eck, R. Dronskowski, M. Takahashi, S. Kikkawa, J. Mater. Chem. 9 (1999) 1527.
[17] K. Suzuki, T. Kaneko, H. Yoshida, H. Morita, H.J. Fujimori, J. Alloys Compd. 224 (1995) 232.
[18] D.J. Kim, Phys. Rev. Lett. 47 (1981) 1213.
[19] R.F. Sabiryanov, S.S. Jaswal, Phys. Rev. Lett. 83 (1999) 2062.
[20] (a) J.P. Perdew, K. Burke, M. Emzerhof, Phys. Rev. Lett. 77 (1996) 3865;
(b) H. Hua, X. Chen, W.A. Goddard III, Phys. Rev. B 55 (1997) 16.
[21] S. Baroni, A.D. Corso, S. Gironcoli, P. Giannozzi, http://www.pwscf.org.
[22] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[23] S. Baroni, S. Gironcoli, D. Corso, P. Giannozzi, Rev. Mod. Phys. 73 (2001) 515.
[24] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 50 (1944) 667.
[25] G. Travaglini, F. Marabelli, R. Monnier, E. Kaldis, P. Wachter, Phys. Rev. B 34 (1986) 3876.
[26] G.A. Samara, P.S. Peercy, in: H. Ehrenreich, F. Seitz, D. Turnbull (Eds.), Solid State Physics, vol. 36, Academic, New York, 1981, p. 1.
[27] H. Das, U.V. Waghmare, T. Saha-Dasgupta, D.D. Sharma, Phys. Rev. Lett. 100 (2008) 186402.