

A first-principles study of elastic, magnetic, and structural properties of PrX_2 ($X=\text{Fe, Mn, Co}$) compounds



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ABSTRACT

The elastic, magnetic, and structural properties of PrX_2 ($X=\text{Fe, Mn, Co}$) alloys, of the cubic Laves structure (MgCu_2), have been evaluated by first-principles density functional theory using both local spin density (LSDA) and generalized gradient (GGA) approximations. The lattice constant, magnetic moment, density of states, band structure, bulk modulus and its first pressure derivative are calculated. At zero pressure, the total magnetic moments of PrFe_2 , PrCo_2 , and PrMn_2 using GGA are 4.515, 1.05, and 4.79 μ_B respectively. The bulk moduli using LSDA are higher than those using GGA approximation. The evaluated Bulk moduli of PrFe_2 , PrMn_2 and PrCo_2 using GGA approximation are 48.1, 42.98, and 72.23 GPa respectively. The lattice constant and magnetic moment of PrFe_2 using GGA approximation are 7.2 Å and 4.51 μ_B respectively in good agreement with experimental results.

1. Introduction

PrX_2 compounds with X (Fe, Mn, Co), which crystallize in the cubic laves structure MgCu_2 type, are interesting materials because of their large magnetic moments, high Curie temperatures [1], and anisotropy, which arise from the rare earth Pr sublattice. In MgCu_2 , there are eight formula units per unit cell and the space group is $Fd\bar{3}m$ as shown in Fig. 1. Generally, the rare earth intermetallic compounds exist in several compositions with varied magnetic properties. High magnetic moment of these compounds is the cause of their importance in many applications; especially those compounds which have a high magnetostriiction. RFe_2 compounds (R: a rare-earth element) have attracted the interest of many researchers e.g. Kubaschewski [2], Cannon et al. [3], and Shimotomai et al. [4]. Kubaschewski and Cannon et al. reported that PrFe_2 cubic phase is formed at high pressure as an equilibrium phase. They found that the lattice parameter of PrFe_2 compound in this MgCu_2 structure is 7.467 Å. Mansey et al. [5] have reported that it is impossible to form this phase, under their experimental conditions, at normal atmospheric pressure. An experimental study by Shimotomai et al. [4] reported on synthesizing the PrFe_2 (C15) phase at 55 kbar. This phase can also be formed by quenching the melt at 7.7 GPa. Tian et al. [6] using heat treatment at 600 °C, have not observed any PrFe_2 phase. Wang et al. [7] have studied the intermetallic phase of SmFe_2 and NdFe_2 . They concluded that SmFe_2 phase is stable and that NdFe_2 phase does not exist. Some compounds of this rare earth family have been reported to crystallize in orthorhombic CeCu_2 -type structure as

PrCu_2 [8]. The intermetallic cubic laves (Pr, Nd, Sm, Tb) Co_2 have been studied by Ponkratze et al. [9], who observed using energy dispersive X-ray diffraction, that there is no structural phase transitions for any one of these compounds up to 40 GPa. The pressure effect on the phase stability was calculated for PrCu_2 by Naka et al. [8], who determined the lattice constant of the orthorhombic PrCu_2 as a function of pressure up to 4 GPa. The rare-earth cobalt intermetallics RCO_2 , have interesting magnetic properties as reported in many studies [9–21]. Theoretical investigation of the electronic structure of the PrCo_x ($x=2, 3$ and 5) compounds has been performed by using the local approximation of the density functional theory scheme, implemented in the projector-augmented wave method by Younsi et al. [22]. The electronic structure of PrCo_2 calculated by K. Younsi et al. showed that a charge transfer took place from Pr to the 3d shell of Co. This results in more stability of the non-spin polarized state of PrCo_2 . Younsi et al. [22] however reported on discrepancies between experimental work of de Jongh et al. [33] and their work. For example, PrCo_2 showed a ferromagnetic order with $T_c=50$ K, yet their calculation indicated that its stable phase is the paramagnetic phase with zero magnetic moment. They, have related these discrepancies to some limitations in their ab initio work.

In this study, we undertake a first-principles calculation of the magnetic, structural, and elastic properties of PrFe_2 , PrMn_2 , PrCo_2 compounds in the MgCu_2 phase, which might be stabilized by suitable experimental conditions. We should emphasize that there are no references, up to our knowledge, for the elastic properties of PrFe_2 and PrMn_2 . There is no reported theoretical or experimental studies on

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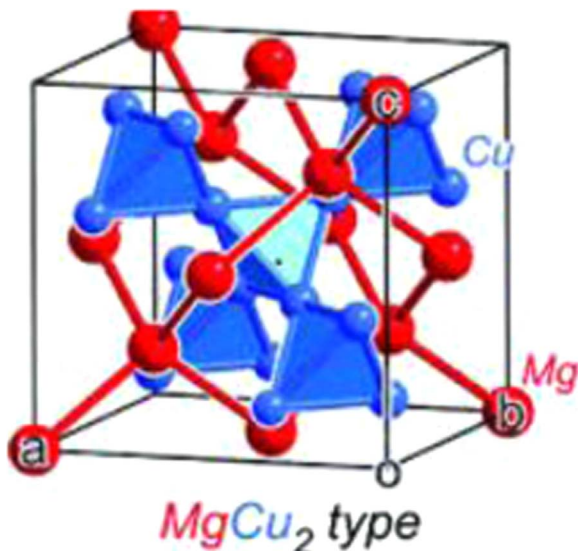


Fig. 1. MgCu₂ crystal structure.

the magnetic moment dependence on pressure for these PrFe₂, PrCo₂, and PrMn₂ alloys, to compare with.

2. Theory and computation

Our calculation is a first-principles study of elastic, magnetic, and structural properties of PrX₂ compounds with X (Fe, Mn, Co) within the framework of density functional theory (DFT) [23,24]. The theoretical values of equilibrium lattice constant, magnetic moment, bulk modulus and its pressure derivative are calculated from the electronic structure by the full-potential non orthogonal local-orbital minimum basis method (FPLO) [25] using both local spin density (LSDA) [26,27] and the generalized gradient approximations (GGA) [28]. The parameters used in the calculation are: the k-mesh subdivision: 24×24×24, the precision of the density and total energy are 10⁻⁶ Å³ and 10⁻⁸ Hartree respectively. These compounds crystallize in the cubic laves phase structure MgCu₂ which has 8 Mg atoms and 16 Cu atoms. The Wyckoff positions in this structure are: the Pr atoms occupy the 8a sites (0, 0, 0) and the X atoms occupy the 16d sites (0.625, 0.625, 0.625). The space group of this structure is F_{D3M} (#227). We have used the Vxc-version of Perdew Bruke Ernzerhof 96 for GGA and Perdew and Zunger method for LSDA. The bulk modulus and its pressure derivative have been computed using the modified Birch-Murnaghan equation of state [29,30]. We have used Eq. (1) in fitting volume vs. energy data obtained from our ab-initio calculation:

$$E(V) = E_0 + \frac{9B_0V_0}{16} \left[B_1 \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\}^3 + \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\}^2 \left\{ 6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right\} \right] \quad (1)$$

and the pressure is given by

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4} (B_1 - 4) \left(\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right) \right] \quad (2)$$

Where, V_0 is equilibrium volume, E_0 is equilibrium energy, B_0 is bulk modulus, and B_1 is pressure first derivative of B_0 .

3. Results and discussion

We have performed ab-initio calculation of the lattice constant and the magnetic properties of PrX₂ compounds with X: Fe, Mn, and Co using the GGA and LSDA approximations. The lattice constants of

PrFe₂, PrCo₂, and PrMn₂ are listed in Table 1. Using GGA approximation, to predict the lattice constant of PrFe₂ is more accurate and closer to experimental results than LSDA results. Up to our knowledge, there are no much available results about PrCo₂ and PrMn₂, because of the difficulty in stabilizing them experimentally. Many studies showed that PrFe₂ compound cannot be synthesized at ambient pressure due to the fact that the ionic radius ratio of Pr: Fe in this compound is larger than the ideal atomic radius ratio for Laves phase compound (1.225) [31]. We have calculated the total magnetic moment of PrFe₂, at ambient pressure using LSDA and GGA approximations to be 1.82 and 4.51 μ_B respectively. Li et al. [32] have reported on experimental work on pseudobinary compounds Pr_xTb_{1-x}Fe₂. They reported a magnetic moment of 4.93 μ_B per formula unit for PrFe₂. L.J. de Jongh et al [33] have experimentally found out that the saturation moment of PrCo₂ at 4.2 K is 3.9 μ_B per formula unit, using the magnetization curve measured in a pulsed-field magnet up to B = 30 T.

The bulk moduli and their pressure derivative of these compounds are listed in Table 2. Energy-optimization curves of PrFe₂, PrMn₂, and PrCo₂ using LSDA and GGA approximations are showing in Figs. 2–4. We have calculated the minimum energy of PrFe₂, PrMn₂, and PrCo₂ using GGA approximation to be -23,576.818, -23,119.182, and -24,059.452 Hartree respectively. We have calculated the total density of states of PrFe₂, PrMn₂, and PrCo₂ compounds as shown in Fig. 5(a,b,c). From these data, it is clear that these compounds are metallic with a high density of states at E_f, especially in the spin-up channel. Using either LSDA or GGA approximations has no effect on the metallicity of these compounds, it only affects the value of density of states at E_f. Now it is important to study the effect of applying high pressure on the total and partial magnetic moments of these compounds. Below the Fermi level, the transition metal band is completely filled by accommodating electrons from the rare earth elements through charge transfer and hybridization. Unoccupied f-levels will be found above the Fermi level [6]. The additional f-electrons of Pr atom would be placed in the narrow band state above the forbidden gap. We concluded that the bulk moduli of these compounds are almost similar, because of the considerable similarity between density of

Table 1

The lattice constants, the total and partial magnetic moments of Pr₂X compounds using both LSDA and GGA approximations.

	a (Å°)		a (Å°)	m (μ _B)		m _i (μ _B)
	LSDA	GGA		LSDA	GGA	
PrFe ₂	6.85	7.2	7.46 [32]	1.82 ^{tot} 0.44 ^{Pr} 0.60 ^{Fe}	4.51 ^{tot} 1.39 ^{Pr} 1.54 ^{Fe}	4.93 [32]
PrCo ₂	6.85	7.15	7.188 [22]	1.15 ^{tot} 1.89 ^{Pr} -0.38 ^{Co}	1.05 ^{tot} 2.24 ^{Pr} -0.59 ^{Co}	3.75 [33], 0.0 [22]
PrMn ₂	6.9	7.3	–	1.37 ^{tot} 0.87 ^{Pr} 0.25 ^{Mn}	4.79 ^{tot} 1.46 ^{Pr} 1.66 ^{Mn}	–

Table 2

The bulk modulus and its first pressure derivative of Pr₂X compounds using both LSDA and GGA approximations.

	B ₀ (GPa)		B ₁	B ₁		Ref.
	LSDA	GGA		Ref.	LSDA	
PrFe ₂	82.73	48.1	–	5.84	3.57	–
PrCo ₂	86.93	72.23	82 [9]	4.95	5.44	3.8 [9]
PrMn ₂	83.69	42.977	–	4.95	4.24	–

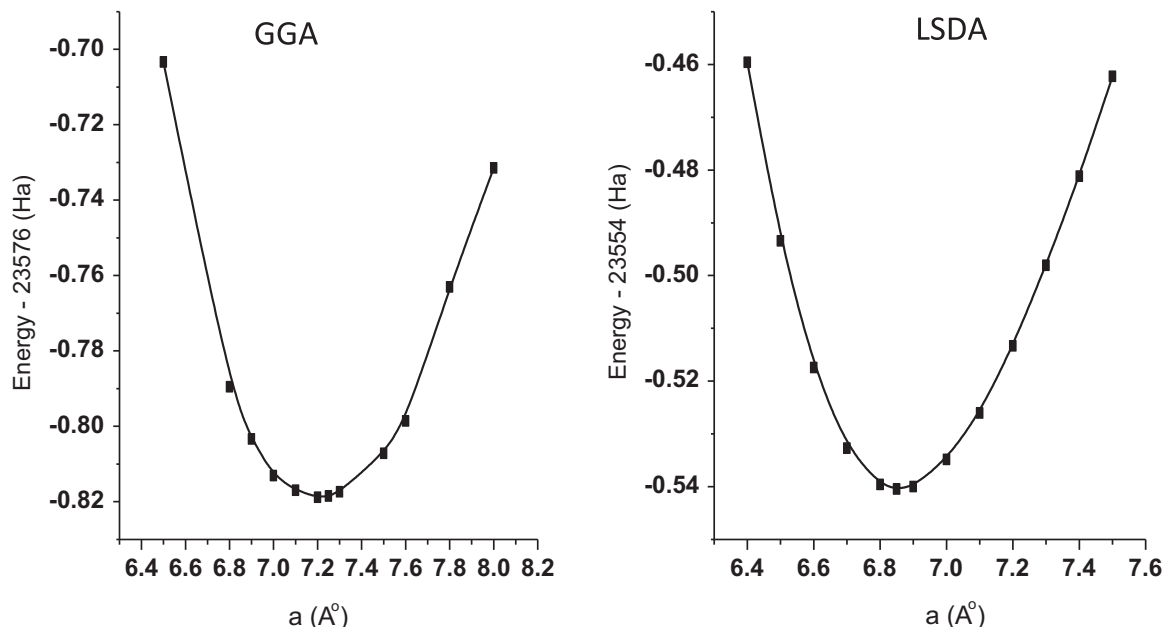


Fig. 2. The minimization energy curve of PrFe_2 using LSDA and GGA approximations.

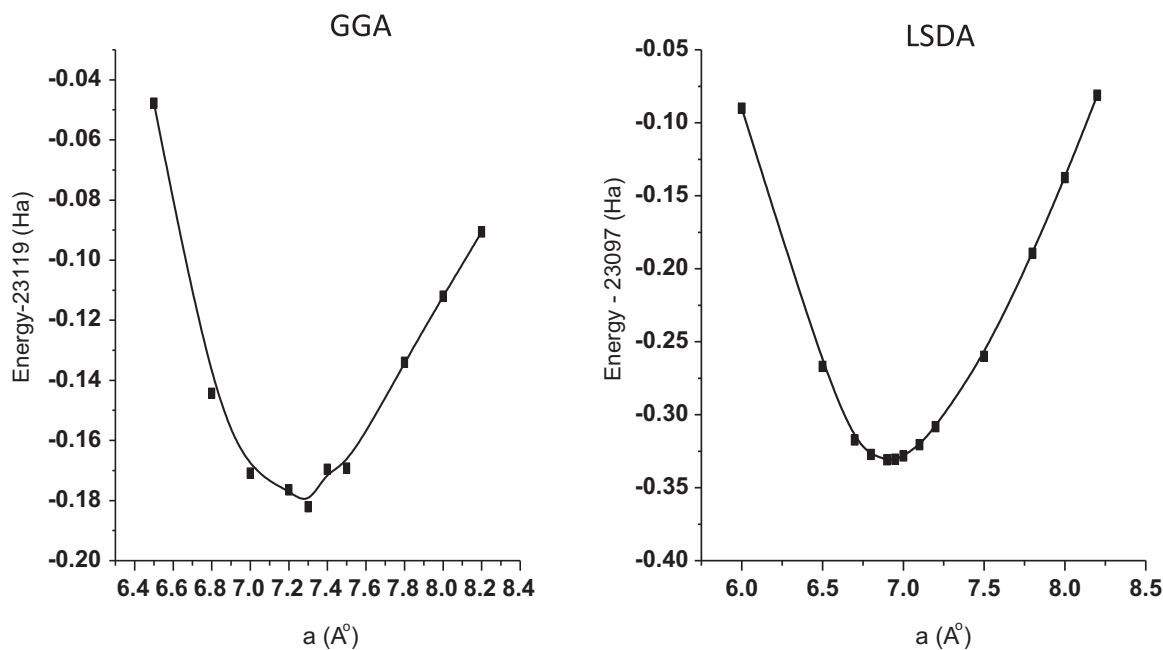


Fig. 3. The minimization energy curve of PrMn_2 using LSDA and GGA approximations.

states. Figs. 6 and 7, display the pressure-dependence of the total and partial magnetic moments of Pr and Co atoms in PrCo_2 using, respectively the LSDA and GGA approximations. By increasing the pressure up to nearly 80 GPa (Fig. 6), the total and Pr-atom magnetic moments decrease, whereas the Co moment decreases, from about $-0.05 \mu_B$, to a very small value. At zero pressure, the Pr-atom moment is higher than the total moment by nearly $0.7 \mu_B$ and persists to be higher than the total moment in the whole pressure range. It is clear that the Pr-atom, by large, is responsible for the magnetic behavior of this ferrimagnetic compound. Upon applying a pressure > 60 GPa on PrCo_2 (Figs. 6 and 7), the magnetic moment of Co turns to be negligibly small. Figs. 8 and 9, display the pressure effect on the magnetic moments of PrFe_2 compound. We conclude from these figures, that PrFe_2 is ferromagnetic compound. In both LSDA and GGA approxima-

tions, the total magnetic moment is higher than Pr and Fe atoms moments. The magnetic moments of Pr and Fe atoms are antiparallel to each other at pressures higher than about 45 GPa and 25 GPa using GGA and LSDA approximations respectively. There are two intercept points between the Pr and Fe atoms moments in these two graphs of pressure vs. magnetic moments. Such intercepts in the magnetic moment dependence on pressure have been reported before [34]. We therefore conclude that PrFe_2 has a ferromagnetic order in the pressure range studied. We assume the cubic Laves structure to be the stable phase of PrFe_2 at ambient pressure in the present study. If we neglect some special cases, e.g. strongly correlated systems, applying a high pressure normally increases orbital overlap and may cause band expansion [35]. Figs. 10 and 11, present the dependence of total and partial moments of PrMn_2 on pressure, using the LSDA and GGA and

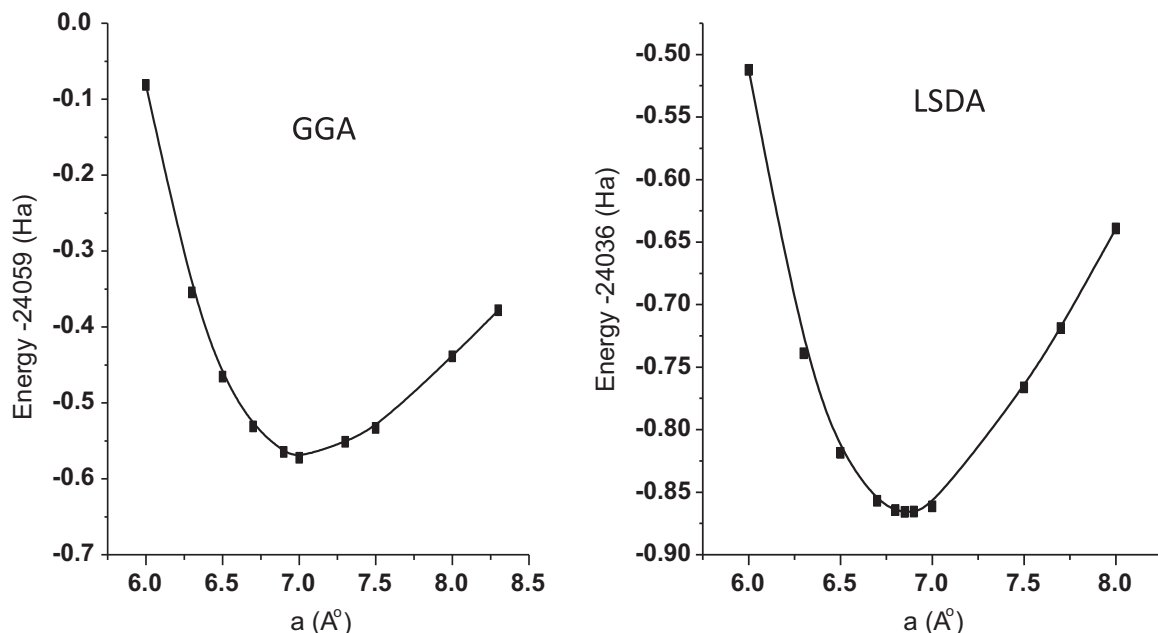


Fig. 4. The minimization energy curve of PrCo₂ using LSDA and GGA approximations.

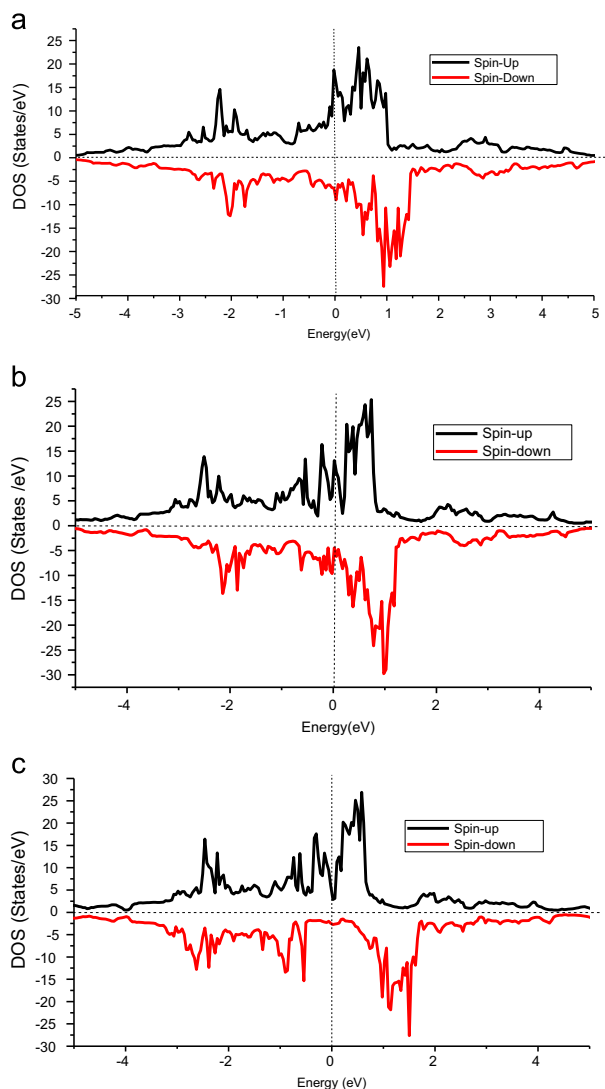


Fig. 5. (a) The DOS of PrMn₂ using LSDA approximation. (b) The DOS of PrFe₂ using LSDA approximation. (c) The DOS of PrCo₂ using LSDA approximation.

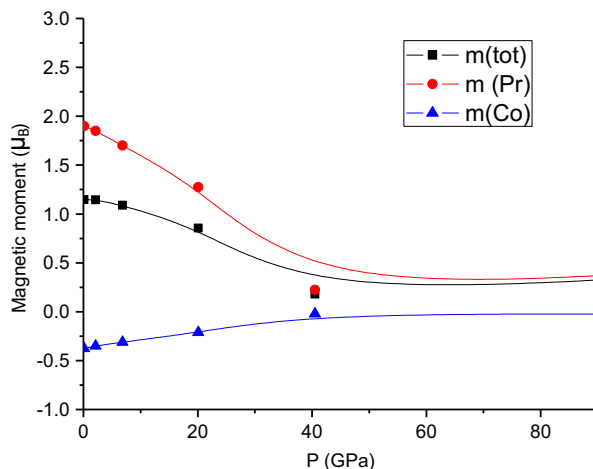


Fig. 6. Pressure vs. total and partial magnetic moments of Pr and Co atoms in PrCo₂ compound using LSDA approximation.

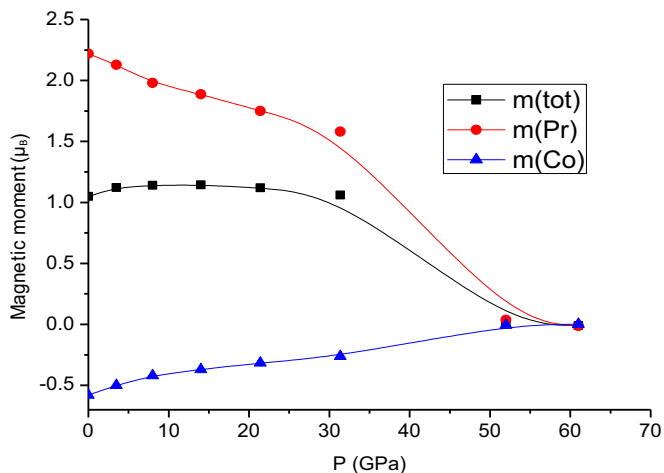


Fig. 7. Pressure vs. total and partial magnetic moments of Pr and Co atoms in PrCo₂ compound using GGA approximation.

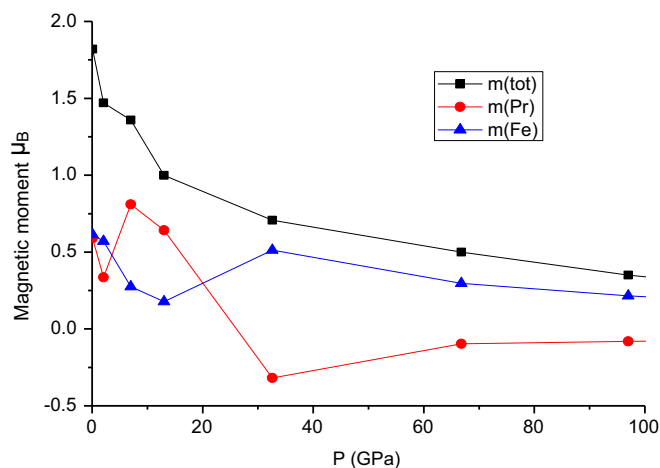


Fig. 8. Pressure vs. total and partial magnetic moments of Pr and Fe atoms in PrFe_2 compound using LSDA approximation.

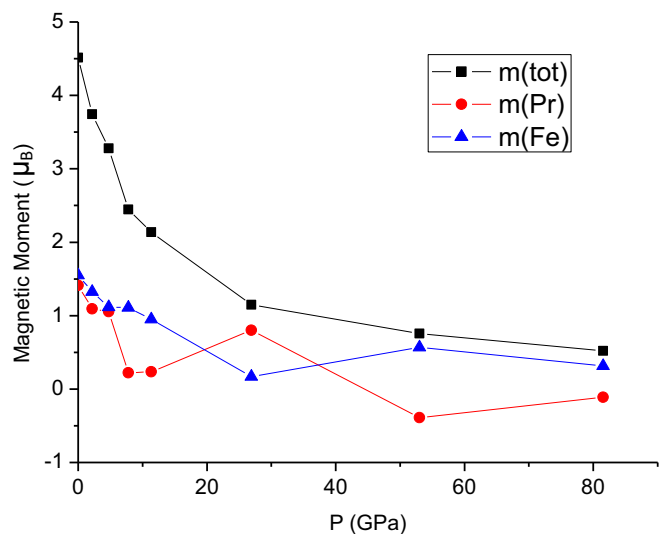


Fig. 9. Pressure vs. total and partial magnetic moments of Pr and Fe atoms in PrFe_2 compound using GGA approximation.

approximations respectively. From these two figures, we observe the tendency of the total magnetic moment to decrease upon increasing the pressure. We have found that the magnetic moment of Pr atom is antiparallel to both of the total and Mn atom moments in the pressure range above ~ 5 and 20 GPa pressure respectively. Below these pressures, the magnetic order of PrFe_2 ferromagnetic. Up to our knowledge, there is no experimental or theoretical data for the effect of pressure on the magnetic properties of these compounds to compare with.....

4. Conclusions

For PrX_2 compounds, which crystallize in the cubic laves structure MgCu_2 with X (Fe, Mn, Co), we have calculated the lattice constant, magnetic moment, its pressure dependence and bulk modulus using both of the LSDA and GGA approximations. The total magnetic moments, at ambient pressure, of PrFe_2 , PrCo_2 , and PrMn_2 , using the GGA approximation, are: 4.51 , 1.05 , and $4.79 \mu_B$ respectively. The electronic structure, in either approximation, confirms the metallicity of the compounds studied. The magnetic moment-pressure dependence of the three systems showed different types of magnetic order. For example a ferrimagnetic coupling is suggested in PrCo_2 up to ~ 60 GPa in both approximations. The other two compounds showed, however ferri/ferromagnetic order within certain pressure ranges. A

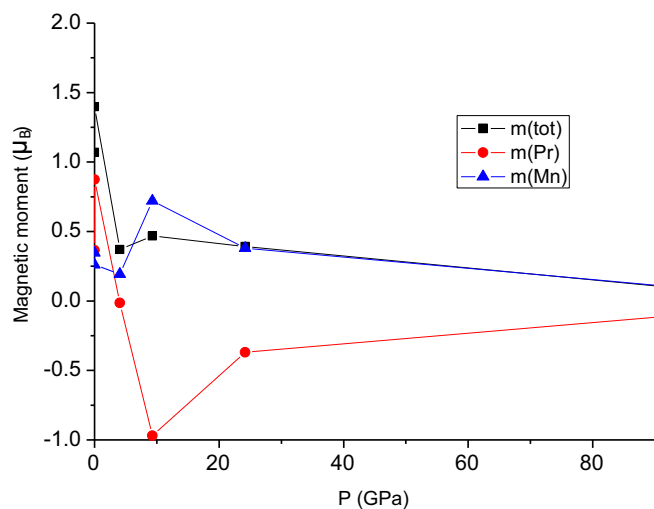


Fig. 10. Pressure vs. total and partial magnetic moments of Pr and Mn atoms in PrMn_2 compound using LSDA approximation.

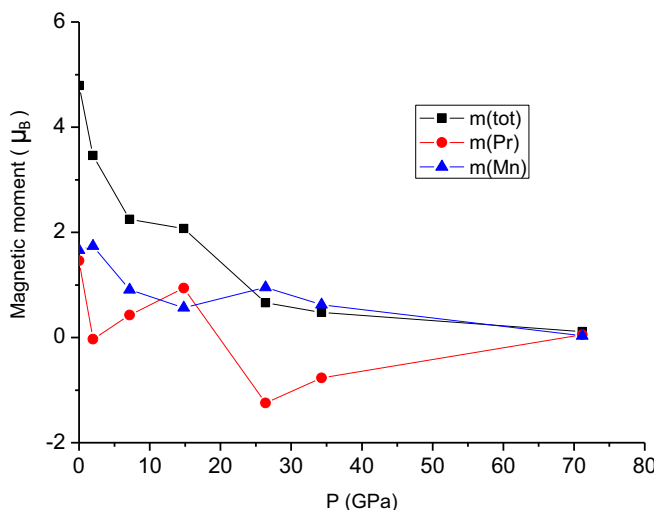


Fig. 11. Pressure vs. total and partial magnetic moments of Pr and Mn atoms in PrMn_2 compound using GGA approximation.

common feature of the magnetic moment-pressure dependence is the decline of the total moment, of the three compounds, as the pressure increases.

References

- [1] K.H.J. Buschow, Rep. Prog. Phys. 40 (1977) 1179.
- [2] O. Kubaschewski, Iron-Binary Phase Diagrams, Springer, Berlin, 1982.
- [3] J.F. Cannon, D.L. Robertson, H.T. Hall, Mater. Res. Bull. 7 (1972) 5.
- [4] M. Shimotomai, M. Doyama, J. Magn. Magn. Mater. 31–34 (1983) 215.
- [5] R.C. Mansey, G.V. Raynor, I.R. Harris, J. Less-Common Met. 14 (1968) 329–336.
- [6] J. Tian, Y. Huang, J. Liang, The Pr-Fe-B ternary system, Sci. Sin. 30 (1987) 607–619.
- [7] B.W. Wang, W.J. Lee, J.S. Song, B.K. Min, Y.M. Hao, J. Appl. Phys. 91 (2002) 9246.
- [8] T. Naka, L.A. Ponomarenko, A. de Visser, A. Matsushita, R. Settai, Y. Onuki, Phys. Rev. B 71 (2005) 024408.
- [9] U. Ponkrat, F. Porsch1, G. Wortmann, W.B. Holzapfel, J. Alloy. Compd. 359 (2003) 99.
- [10] D. Gignoux, F. Givord, R. Lemaire, Phys. Rev. B 12 (1975) 3878.
- [11] D. Gignoux, D. Givord, F. Givord, W.C. Kohler, R.M. Moon, Phys. Rev. B 14 (1976) 162.
- [12] D. Gignoux, F. Givord, W.C. Kohler, Physica B 86–88 (1977) 165.
- [13] S. Hirotsawa, Y. Nakamura, J. Phys. Soc. Jpn. 51 (1982) 2464.
- [14] S. Hirotsawa, Y. Nakamura, J. Phys. Soc. Jpn. 51 (1982) 2819.
- [15] H. Mitamura, T. Sakakibara, T. Goto, H. Yamada, J. Magn. Magn. Mat. 140 (1995) 821.
- [16] N.H. Duc, T.D. Hien, P.E. Brommer, J.J.M. Franse, J. Magn. Magn. Mat. 104 (1992) 1252.

- [17] N.H. Duc, T.D. Hien, D. Givord, J.J.M. Franse, F.R. de Boer, *J. Magn. Magn. Mat.* 124 (1993) 305.
- [18] N.H. Duc, T.D. Hien, *J. Magn. Magn. Mat.* 140 (1995) 823.
- [19] I.S. Dubenko, R.Z. Levitin, A.S. Markosyan, V. von Snegirev, A.Yu Sokolov, *J. Magn. Magn. Mat.* 140 (1995) 825.
- [20] N. Baranov, E. Gratz, H. Nowotny, W. Steiner, *J. Magn. Magn. Mat.* 37 (1983) 206.
- [21] L.B. Chiu, P.R. Elliston, A.M. Stewart, K.N.R. Taylor, M.A.A. Issa, *J. Phys. F: Met. Phys.* 10 (1980) 2297.
- [22] K. Younsi, J.C. Crivello, V.P. Boncour, L. Bessais, F. Porcher, G. Andre, *J. Phys.: Condens. Matter* 25 (2013) 116001.
- [23] R.G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
- [24] R.M. Dreizler, J. da Providencia, *Density Functional Methods in Physics*, Plenum, New York, 1985.
- [25] I. Ophale, K. Koepernik, H. Eschrig, *Phys. Rev. B* 60 (1999) 1403.
- [26] S. Lundqvist, N.H. March, (Eds.), *Theory of the Inhomogeneous Electron Gas*, Plenum, New York, 1983.
- [27] J. Gallaway, N.H. March, *Solid State Phys.* 38 (1984) 135.
- [28] J.P. Perdew, W. Yue, *Phys. Rev. B* 33 (1986) 8800 (R).
- [29] F. Birch, *Phys. Rev.* 71 (1947) 809.
- [30] F. Birch, *J. Geophys. Res.* 83 (1978) 1257.
- [31] H.Y. Liu, F.B. Meng, S.T. Li, Y.X. Li, J.L. Chen, G.H. Wu, *Physica B* 351 (2004) 102–105.
- [32] Y. Li, C. Tang, J. Du, G. Wu, W. Zhan, W. Yan, G. Xu, Q. Yang, *J. Appl. Phys.* 83 (1998) 7753.
- [33] L.J. de Jongh, J. Bartolomé, F. Greidanus, H. de Groot, H. Stipdonk, K.H.J. Buschow, *J. Magn. Magn. Mat.* 25 (1981) 207.
- [34] S.H. Aly, R.M. Shabara, *J. Magn. Magn. Mat.* 360 (2014) 143.
- [35] R. Demchyna, S. Leoni, H. Rosner, U. Schwarz, *ZKRI* 221 (2006) 420.