Magnetic collapse in Fe$_3$Se$_4$ under high pressure

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Abstract: Electronic structure and magnetic properties of Fe$_3$Se$_4$ are calculated within the density functional approach. Due to the metallic properties, magnetic moments of the iron atoms in two nonequivalent positions in the unit cell are different from ionic values for Fe$^{3+}$ and Fe$^{2+}$ and are equal to $M_1 = 2.071\mu_B$ and $M_2 = −2.042\mu_B$ making the system ferrimagnetic. The total magnetic moment for the unit cell is $2.135\mu_B$. Under the isotropic compression, the total magnetic moment decreases non-monotonically and correlates with the non-monotonic dependence of the density of states at the Fermi level $N(E_F)$. For 7% compression, the magnetic order changes from the ferrimagnetic to the ferromagnetic. At 14% compression, the magnetic order disappears and the magnetic moment becomes zero. This compression corresponds to the pressure of 114 GPa. The system remains in the metallic state for all values of compression.

Keywords: Band structure; Magnetic moment; DFT; Pressure; Ferrimagnet; Ferromagnet; Iron selenide

PACS: 62.50.-p, 71.15.Mb, 75.50.Gg, 75.50.Bb

1. Introduction

Magnetic collapse associated with the disappearance of magnetic moments in 3$d$ ions is observed in many insulating transition metal oxides (Mn-O, Fe-O, Co-O, Ni-O). A review of experimental data for iron oxides [1] revealed that the spin crossover between the high-spin and low-spin states of the cation in most cases takes place with the increasing pressure and the critical pressure is close to 50-70 GPa. The crystals with Fe$^{2+}$ ions have a low-spin state with a zero spin ($S = 0$) that leads to the appearance of a non-magnetic phase. In the case of crystals with Fe$^{3+}$ ions, the low-spin state exhibit $S = 1/2$, so the magnetic state can be preserved albeit at a lower critical temperature such as in FeBO$_3$ [2]. For magnetite Fe$_3$O$_4$ containing both Fe$^{2+}$ and Fe$^{3+}$ ions, a new non-magnetic phase was experimentally found [3,4] at pressures above 25 GPa and at a room temperature.

The iron selenides FeSe$_x$ ($1 \leq x \leq 1.33$) form phases with iron vacancies that crystallize into structures derived from the hexagonal NiAs-type structure. Among them two compounds, Fe$_7$Se$_8$ and Fe$_3$Se$_4$, have superstructure with ordered Fe vacancies [5]. Fe$_7$Se$_8$ has a hexagonal structure whereas Fe$_3$Se$_4$ has a monoclinic structure isomorphic to Cr$_3$X$_4$ (X=S, Se, Te). In a Fe$_3$Se$_4$ unit cell, the vacancies of Fe appear in every second iron layer. The presence of ordered Fe vacancies facilitates the appearance of the ferrimagnetic state in Fe$_3$Se$_4$ [6–9]. The experimental values of the total magnetic moment are in the range from 0.69$\mu_B$ to 1.17$\mu_B$ per formula unit (f.u.) [6–8]. The magnetic moments on Fe ions estimated within the framework of the ionic model [7] are too large ($3.25\mu_B$ for site 1 and $1.94\mu_B$ for site 2) and are not validated by experimental data [7,9,10]. Neutron diffraction on Fe$_3$Se$_4$ gives smaller effective spin values for two Fe positions, $S_1 = 1.08\mu_B$ and $S_2 = 0.71\mu_B$ [10]. In addition, Mössbauer study revealed the very low average internal magnetic fields for Fe sites [9], which do not correspond to regular high-spin Fe$^{3+}$ or Fe$^{2+}$ states. All of the mentioned above indicates the delocalization of 3$d$ electrons of iron ions and the inapplicability of the model of localized magnetic moments to the system.
In the series Fe$_3$O$_4$–Fe$_3$S$_4$–Fe$_3$Se$_4$, on the one hand, the presence of two non-equivalent positions of cations and ferrimagnetic properties are preserved, on the other hand, an increase in covalence enhances the metallic properties. Despite the structural similarity between greigite Fe$_3$S$_4$ and magnetite Fe$_3$O$_4$, their magnetic properties [11] and magneto-optical spectra [12] differ significantly. The differences from magnetite become even greater for Fe$_3$Se$_4$, which has interesting magnetic and electrical properties [8–10]. Fe$_3$Se$_4$ is a metallic ferrimagnetic material. Its electronic structure was calculated within the density functional theory (DFT) [13]. Tewari et al. [6] declare that the Fe$_3$Se$_4$ material possesses half-metallic properties. The spin-down band gap ($E_g$) and half-metallic energy gap ($E_{HM}$) calculated using the HSE06 hybrid functional [14] were found to be 1.8 eV and 0.17 eV, respectively. However, the analysis of experimental data revealed the extremely small $E_{HM}$ (1.3 meV and 34 meV, depending on the Se stoichiometry), thus the low energy is required to occupy minority spin states by the majority spin carriers during spin flip processes. The discrepancy between the theoretical and experimental $E_{HM}$ values can be associated with an increase in the localization of electronic states when a fraction of the Hartree-Fock exchange energy is included. This results in the inaccurate description of electronic structure near the Fermi level. It is known that HSE06 functional can overestimate the band gap [15,16]. Moreover, Gao et al. [17] suggest that hybrid functionals, such as HSE and PBE0 are not suitable for studying metal systems and the LDA or GGA give better results in describing metallic properties.

Here we study the properties of Fe$_3$Se$_4$ under high pressure within DFT. We calculated the changes of the magnetic moment on each sublattice with the increasing isotropic compression. The values of the magnetic moments decrease non-monotonically and eventually vanish for both inequivalent positions. Since Fe$_3$Se$_4$ possess metallic properties, such a magnetic collapse cannot be represented as the energy-level crossing of the high-spin and the low-spin cation states. In this case, the magnetic collapse is caused by the alignment of the numbers of spin-up and spin-down electrons on each cation so one can call this the itinerant analogue of the spin crossover.

### 2. Computational details

Calculations of atomic and electronic structure and magnetic properties were performed in the framework of density functional theory using the Vienna ab-initio simulation package (VASP) [18]. Exchange-correlation effects were described by the Perdew-Burke-Ernzerh (PBE) of generalized gradient approximation (GGA) [19]. The ion-electron interactions were represented by the projector-augmented wave method (PAW) [20] and the plane-wave cutoff energy of 600 eV was applied. The criteria for the total energy minimization and interatomic forces were set to $10^{-4}$ eV and $10^{-2}$ eV/Å, respectively. The energy convergence criteria were decreased to $10^{-5}$ eV to obtain a more accurate electronic structure. The first Brillouin zone (1BZ) was sampled by $24 \times 14 \times 8$ grid using the Monkhorst-Pack scheme [21]. The Visualization for Electronic and Structural Analysis (VESTA) [22] software was used for representation of atomic structures. The “vaspkit” software [23] was used for post-processing.

### 3. Results and discussion

The crystal structure of the bulk Fe$_3$Se$_4$ is shown in Fig. 1(a). The unit cell relates to the $I2/m$ space group with the structural parameters $a = 6.071$ Å, $b = 3.377$ Å, $c = 11.174$ Å, and $\beta = 92.818^\circ$, which are in good agreement with previously reported experimental data [6,9,10], see Table 1 for comparison. The unit cell contains six Fe atoms and eight Se atoms, with iron atoms occupying two non-equivalent positions, namely, octahedral (Fe$_2$) and distorted octahedral (Fe$_1$) sites. Fe$_2$-Se bond lengths are 2.468 Å and 2.413 Å and Fe$_1$-Se bond lengths are 2.390 Å, 2.374 Å, 2.545 Å, and 2.581 Å (Table 2). The distances between Se atoms closest to the iron vacancy are 2.996 Å and 5.277 Å. The magnetic structure was found to be ferrimagnetic.
Figure 1. Atomic structure (a) and density of states (b,c) of Fe$_3$Se$_4$. In panel (a), brown and yellow-green colors correspond to Fe and Se atoms, respectively. Total DOS of Fe$_3$Se$_4$ is shown by black curves. In panel (b), partial DOS of Fe and Se atoms are shown by green and red curves, respectively. In panel (c), partial DOS of iron atoms on site 1 and on site 2 are shown by green and red curves, respectively. Positive and negative values of DOS corresponds to spin-up and spin-down channels, respectively. The Fermi level corresponds to zero.

The total magnetic moment is 2.135µ$_B$/f.u. that is in the range of the previously DFT calculated values [6,13,24] but larger than the known experimental values [6–8], see Table 1. The discrepancy in magnetic moment between experimental and DFT predicted values relates to the delocalization of 3$d$ electrons of Fe ions. The calculated magnetic moment on iron in sites 1 and 2 are 2.071µ$_B$ and −2.042µ$_B$, respectively. Our calculations showed that the electronic structure of Fe$_3$Se$_4$ is metallic, see Fig. 1(b,c), as in the [13,25] and half-metallic state was not found. The density of states (DOS) at the Fermi level are predominantly formed by iron states. The bulk modulus of Fe$_3$Se$_4$ is determined by performing six finite distortions of the lattice with ±0.5, ±1.0, ±1.5% magnitude. The calculated P – V data are fitted to the Birch–Murnaghan equation of state $P = 3/2B_0 \left[ u^{7/3} - u^{-5/3} \right] \cdot \left[ 1 - 3/4(4 - B') (u^{-2/3} - 1) \right]$, where $B_0$, $u = V/V_0$, $V_0$, $V$, and $B'$ are the bulk module, the dimensionless volume, the reference volume (the initial volume of Fe$_3$Se$_4$), the deformed volume, and the derivative of the bulk modulus with respect to pressure, correspondingly. Bulk modulus as a function of volume is shown at Fig. 2. The obtained value of $B_0$ is 68 GPa, which is very similar to that of Fe$_3$S$_4$ (62.8 GPa) [26] and is in the range of values for isomorphic Cr$_3$Se$_4$ (57.7 GPa) and Cr$_3$S$_4$ (72.9 GPa) [27] structures. Its pressure derivative was found to be 6.

Next we study the effect of strain on the magnetic and electronic properties of Fe$_3$Se$_4$. The isotropic compressive strain was modelled as the change of the structural parameter, i.e. we set the value of strain as $(l_0 - l)/l_0$, where $l_0$ and $l$ are the equilibrium and strained structural parameters, respectively. Isotropic compression along the lattice constant up to 4% reduces the total magnetic moment of the system to 0.157µ$_B$/f.u., see Fig. 3(a) and Table 2. Further compression to 5% increases the magnetic moment by 0.904µ$_B$/f.u., then the magnetic moment decreases again to 0.124µ$_B$/f.u. (6.5% compression). Compression to 7% leads to a sharp jump in the magnetic moment up to 1.626µ$_B$ and the magnetic order changes from ferrimagnetic to ferromagnetic. The bond lengths of Fe$_3$Se$_4$ under 7% strain is unevenly decreased by 2.26–8.87%. The distances between selenium atoms located near the iron vacancy are reduced by 7.4 and 11.7% compared to the initial distance and equal to 4.888 Å and 2.645 Å, Table 2.
Figure 2. Pressure as a function of Fe$_3$Se$_4$ volume. Blue dots indicate values for structures with finite strains ±0.5, ±1.0, ±1.5%. The curve through this values fitted to the Birch–Murnaghan equation is marked by red.

Figure 3. The dependence of the total magnetic moment (a) and DOS at the Fermi level (b) on compression.
Figure 4. Total (TDOS) and partial (PDOS) densities of states for Fe₃Se₄ under 7% (a) and 14% (b) compression. Positive and negative values corresponds to spin-up and spin-down channels, respectively. The Fermi level corresponds to zero.

Table 1. Structural and magnetic parameters of monoclinic phase of Fe₃Se₄.

| Structural parameters | Magnetic moment (μ_B/f.u.) | Ref. |
|-----------------------|----------------------------|------|
| Lattice constant (Å)  |                            |      |
| a                      | 6.202                      | [9]  |
| b                      | 3.532                      |      |
| c                      | 11.331                     |      |
| β                      | 91.825°                    |      |
| -                      | 6.113                      | [10] |
| -                      | 3.486                      |      |
| -                      | 11.139                     |      |
| -                      | 91.66°                     |      |
| -                      | 6.16                       | [5]  |
| -                      | 3.53                       |      |
| -                      | 11.10                      |      |
| -                      | 92.0°                      |      |
| -                      | 2.128                      | This work |
| -                      | 6.071                      |      |
| -                      | 3.377                      |      |
| -                      | 11.174                     |      |
| -                      | 92.818°                    |      |
**Table 2.** Bond lengths (Å) and distance between Se atoms closest to the iron vacancy of the Fe\textsubscript{3}Se\textsubscript{4} monoclinic phase. The atomic numbering scheme is shown in Fig. 1(a).

| Strain (%) | Bond or distance | Strain (%) | Bond or distance |
|------------|------------------|------------|------------------|
| 0          | 2.468 2.413 2.390 2.374 2.545 2.581 2.996 5.277 | 7          | 2.306 2.245 2.239 2.311 2.379 2.352 2.645 4.888 |
| 14         | 2.143 2.078 2.109 2.189 2.277 2.169 2.292 4.455 |

**Table 3.** Magnetic moments (in $\mu_B$) of iron atoms on two sites, Fe\textsubscript{1} and Fe\textsubscript{2}, and total magnetic moments per Fe\textsubscript{3}Se\textsubscript{4} formula unit of Fe\textsubscript{3}Se\textsubscript{4} under compression.

| Strain (%) | Fe\textsubscript{1} moment | Fe\textsubscript{2} moment | Total moment |
|------------|-----------------------------|-----------------------------|-------------|
| 0          | 2.071 -2.042 2.135           |                             |             |
| 2          | 1.778 -1.631 1.969           |                             |             |
| 3          | 1.556 -1.417 1.759           |                             |             |
| 3.5        | 1.387 -1.318 1.460           |                             |             |
| 4          | 0.602 -1.334 0.157           |                             |             |
| 4.5        | 0.282 -1.214 0.692           |                             |             |
| 5          | 0.764 -0.462 1.061           |                             |             |
| 10         | 0.266 -0.209 0.368           |                             |             |
| 5.5        | 0.493 -0.297 0.673           |                             |             |
| 6.5        | 0.053 -0.041 0.124           |                             |             |
| 7          | 0.463 0.666 1.626            |                             |             |
| 8          | 0.352 0.540 1.286            |                             |             |
| 9          | 0.282 0.425 1.038            |                             |             |
| 10         | 0.225 0.328 0.823            |                             |             |
| 11         | 0.162 0.230 0.585            |                             |             |
| 12         | 0.068 0.094 0.243            |                             |             |
| 13         | 0.004 0.005 0.009            |                             |             |
| 14         | 0.000 0.000 0.000            |                             |             |
The magnetic moment decreases linearly with the further compression from 7% to 13% and vanishes under 14% of compression. The pressure corresponding to this strain is equal to 114 GPa and the volume of the cell is 145.55 Å³. In this structure Fe-Se bond lengths are less by 7.79–15.96% compared to the bond lengths in the original structure. The distances between selenium atoms near the vacancy decrease by 15.6 and 23.5% and are equal to 4.455 Å and 2.292 Å. Values of the iron magnetic moments on sites 1 and 2 are shown in Table 3.

The electronic structure of Fe₃Se₄ remains metallic throughout the studied compression range. The DOS at the Fermi level \( N(E_F) \) as a function of strain is presented at Fig. 3(b). The slight compression up to 3.5% leads to an increase in the density of states at the Fermi level. Further, the \( N(E_F) \) non-monotonically depends on the strain and correlates with the non-monotonic dependance of the total magnetic moment. An increase and decrease in the total magnetic moment is accompanied by an increase and decrease in the \( N(E_F) \). The decrease in the magnetic moment during compression from 8 to 14% is accompanied by an increase in the \( N(E_F) \). Fig. 4 shows DOS of Fe₃Se₄ at critical points. The redistribution of DOSs are observed, compared with the DOS of the original structure Fig. 1(c). The compression up to 7% results to \( N(E_F) \) decreasing, and the vacant states are shifted to higher energies by 0.6 eV. The density of states with spin-up and spin-down is equalized on each Fe cation in the structure at a deformation of 14% (Fig. 4(b)), which leads to the disappearance of the magnetic order. It is the itinerant analogue of the spin crossover in the metallic system. The structure becomes nonmagnetic. In this case, the DOS at the Fermi level is increased. The occupied states decrease significantly at \(-0.25\) eV and increase at lower energies. The vacant states decrease at 0.19 eV and increase at higher energies.

4. Conclusion

DFT calculations within GGA for Fe₃Se₄ shows that the ground state is metallic and the system is not in the half-metal state. That agrees with conclusions of Refs. [13,25]. The value of the bulk modulus was found to be 68 GPa. By studying the effect of strain on Fe₃Se₄ within DFT, we found the itinerant analogue of the spin crossover in the metallic system. In particular, we calculated the magnetic moment in each of two iron sublattices of Fe₃Se₄ with the increasing isotropic compression. The values of the moments decrease non-monotonically and eventually vanish for both inequivalent positions at the 14% of strain that is estimated to correspond to the pressure of 114 GPa. Under the strain, the system evolves from the uncompressed ferrimagnetic state first to the ferromagnetic state and then to the nonmagnetic state; the process sketched in Fig. 5.
Author Contributions: Conceptualization, S.G.O.; calculations, L.V.B.; formal analysis, M.M.K.; writing, L.V.B., S.G.O., and M.M.K.; funding acquisition, S.G.O. All authors have read and agreed to the published version of the manuscript.

Funding: L.V.B. and S.G.O. acknowledge support by Russian Science Foundation (Project 18-12-00022I).

Acknowledgments: We acknowledge useful discussions with M.A. Vysotin. L.V.B. would like to thank Information Technology Center, Novosibirsk State University, for providing the access to supercomputer facilities.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. I. S. Lyubutin and A. G. Gavriliuk, High and Ultra-High Pressure Research on Phase Transformations in 3d-Metal Oxides: Current Progress, Uspekhi Fiz. Nauk 179, 1047 (2009).
2. A. G. Gavriliuk, I. A. Trojan, I. S. Lyubutin, S. G. Ovchinnikov, and V. A. Sarkissian, High-Pressure Magnetic Properties and \( P - T \) Phase Diagram of Iron Borate, J. Exp. Theor. Phys. 100, 688 (2005).
3. H.-K. Mao, T. Takahashi, W. A. Bassett, G. L. Kinsland, and L. Merrill, Isothermal Compression of Magnetite to 320 KB and Pressure-Induced Phase Transformation, J. Geophys. Res. 79, 1165 (1974).
4. M. P. Pasternak, S. Nasu, K. Wada, and S. Endo, High-Pressure Phase of Magnetite, Phys. Rev. B 50, 6446 (1994).
5. A. Okazaki and K. Hirakawa, Structural Study of Iron Selenides Fe\( _3 \)Se\( _4 \). I Ordered Arrangement of Defects of Fe Atoms, J. Phys. Soc. Japan 11, 930 (1956).
6. G. C. Tewari, D. Srivastava, R. Pohjonen, O. Mustonen, A. J. Karttunen, J. Linden, and M. Karppinen, Fe\( _3 \)Se\( _4 \): A Possible Ferrimagnetic Half-Metal?, J. Phys. Condens. Matter 32, 455801 (2020).
7. B. Lambert-Andron and G. Berodias, Etude Par Diffraction Neutronique de Fe\( _3 \)Se\( _4 \), Solid State Commun. 7, 623 (1969).
8. K. Adachi, Magnetic Anisotropy Energy in Nickel Arsenide Type Crystals, J. Phys. Soc. Jpn. 16, 2187 (1961).
9. R. Pohjonen, O. Mustonen, M. Karppinen, and J. Linden, Mössbauer Study of Magnetism in Fe\( _3 \)Se\( _4 \), J. Alloys Compd. 746, 135 (2018).
10. A. F. Andresen, A Neutron Diffraction Investigation of Fe\( _3 \)Se\( _4 \), Acta Chem. Scand. 22, 827 (1968).
11. L. Chang, A. P. Roberts, Y. Tang, B. D. Rainford, A. R. Muxworthy, and Q. Chen, Fundamental Magnetic Parameters from Pure Synthetic Greigite (Fe\( _3 \)S\( _4 \)), J. Geophys. Res. 113, B06104 (2008).
12. I. S. Lyubutin, S. S. Starchikov, C. R. Lin, S. Z. Lu, M. O. Shaikh, K. O. Funtov, T. V. Dmitrieva, S. G. Ovchinnikov, I. S. Edelman, and R. Ivantsov, Magnetic, Structural, and Electronic Properties of Iron Sulfide Fe\( _3 \)S\( _4 \) Nanoparticles Synthesized by the Polyol Mediated Process, J. Nanoparticle Res. 15, 1397 (2013).
13. D. Singh, S. K. Gupta, H. He, and Y. Sonvane, First-Principles Study of the Electronic, Magnetic, and Optical Properties of Fe\( _3 \)Se\( _4 \) in Its Monoclinic Phase, J. Magn. Magn. Mater. 498, 166157 (2020).
14. A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, Influence of the Exchange Screening Parameter on the Performance of Screened Hybrid Functionals, J. Chem. Phys. 125, 224106 (2006).
15. Y. Meng, X. W. Liu, C. F. Huo, W. P. Guo, D. B. Cao, Q. Peng, A. Dearden, X. Gonze, Y. Yang, J. Wang, H. Jiao, Y. Li, and X. D. Wen, When Density Functional Approximations Meet Iron Oxides, J. Chem. Theory Comput. 12, 5132 (2016).
16. J. Noh, O. I. Osman, S. G. Aziz, P. Winget, and J. L. Brédas, A Density Functional Theory Investigation of the Electronic Structure and Spin Moments of Magnetite, Sci. Technol. Adv. Mater. 15, 044202 (2014).
17. W. Gao, T. A. Abetew, T. Cai, Y. Y. Sun, S. Zhang, and P. Zhang, On the Applicability of Hybrid Functionals for Predicting Fundamental Properties of Metals, Solid State Commun. 234-235, 10 (2016).
18. G. Kresse and J. Furthmüller, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set, Phys. Rev. B 54, 11169 (1996).
19. J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).
20. P. E. Blöchl, Projector Augmented-Wave Method, Phys. Rev. B 50, 17953 (1994).
21. H. J. Monkhorst and J. D. Pack, Special Points for Brillouin-Zone Integrations, Phys. Rev. B 13, 5188 (1976).
22. K. Momma and F. Izumi, VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data, J. Appl. Crystallogr. 44, 1272 (2011).
23. V. Wang, N. Xu, J. C. Liu, G. Tang, and W. T. Geng, VASPKIT: A User-Friendly Interface Facilitating High-Throughput Computing and Analysis Using VASP Code, Comput. Phys. Commun. 267, 108033 (2021).
24. G. Long, H. Zhang, D. Li, R. Sabirianov, Z. Zhang, and H. Zeng, Magnetic Anisotropy and Coercivity of Fe\( _3 \)Se\( _4 \) Nanostructures, Appl. Phys. Lett. 99, 2011 (2011).
25. K. Persson, Materials Data on Fe\( _3 \)Se\( _4 \) (SG : 12) by Materials Project, https://materialsproject.org/materials/mp-569176/ (2016).
26. A. Roldan, D. Santos-Carballal, and N. H. de Leeuw, A comparative DFT study of the mechanical and electronic properties of greigite Fe₃S₄ and magnetite Fe₃O₄, J. Chem. Phys. 138, 204712 (2013).

27. S. Guo, and B. Liu, Stable half-metallic ferromagnetism in nonstoichiometric cubic binary chromium chalcogenides, EPL. 88, 67007 (2009).