Ab initio study on magnetism and pressure-induced transitions in cubic MnGe

U. K. Rößler
IFW Dresden, Postfach 270116, D-01171 Dresden, Germany
E-mail: u.roessler@ifw-dresden.de

Abstract. State of the art density functional theory (DFT) calculations within the generalized gradient approximation (GGA) are reported for the (metastable) cubic MnGe with chiral B20 structure under applied pressure. It is found that the ambient pressure metallic (nominally) ferromagnetic high spin state (2 \( \mu_B \)/f.u.) in MnGe undergoes a transition into a low spin state (1 \( \mu_B \)/f.u.). From the calculations, the pressure at this first-order transition is about 18 GPa. The low moment state is halfmetallic, i.e., a small band-gap opens in the density of states for the majority spin electrons at the Fermi edge. Calculations for decreasing lattice parameter show that a fully metallic ferromagnetic low spin state should be recovered, before at still higher pressures the magnetic moment collapses and a non-spin polarized state arises. For the zero, low and high spin states, the equation of state has been determined. As the non-centrosymmetric crystal structure enables chiral Dzyaloshinskii-Moriya couplings, the magnetic order in MnGe is long-period modulated. The theoretical results suggest that half-metallic transport properties could be observed on the background of chiral complex spin-structures in MnGe under pressure or in strained thin films.

1. Introduction
The series of magnetic 3d transition metal – silicides with chiral B20 structure and their alloys, with MnSi as best investigated system, are attracting continuing attention, that derives from their chiral helimagnetism [1, 2, 3] and the possibility to reach a pressure-collapse of their magnetic order [4]. The magnetic properties of MnSi are those of a weakly ferromagnetic metallic system subject to strong spin-fluctuations. Chiral Dzyaloshinskii-Moriya couplings state [5] are responsible for the long-period helimagnetic ground-state [5, 2, 3]. The properties of the analogous germanides are less investigated, owing to their difficult synthesis, but the tendency towards magnetically ordered states is much stronger in this series. For applications and possible integration into spintronics devices, the higher transition temperatures of the germanide series appears promising [6, 7]. The magnetic germanide FeGe with the cubic B20 structure is a chiral helimagnet as MnSi, but the underlying electronic structure is closer to strong band ferromagnetism [8]. A quantum phase transition from the magnetically ordered state to an unconventional paramagnetic Non-Fermi-Liquid (NFL) state has been found at high pressures [9]. Cubic MnGe can be synthesized only under pressure [10, 11]. MnGe is known to undergo a magnetic transition, but information on magnetic order and phase diagram is incomplete. Experimental data report a magnetic ordering temperature 197 K, and from Curie-Weiss fits in paramagnetic state \( \theta_C = 187 \) K \( \mu_{\text{eff}} = 3.0 \ \mu_B \) [10]. The experiments by Kanazawa et al. show a magnetic ordering temperature \( T_N \approx 170 \) K. Magnetization curves at
5 K show technical saturation at magnetic fields $\mu_0 H_{c2} \geq 13$ T only with a moment of about 1.9 $\mu_B$/f.u.[11]. Another anomaly with weak hystereses is seen in a field range 0.5 < $\mu_0 H_{c1}$ < 2 T for temperatures $T < 100$ K, which may indicate a helix reorientation transition or a transition from a low-field, effectively antiferromagnetic, modulated states into an intermediate possibly also modulated state. This magnetization process in applied magnetic field differs not only regarding the large magnitude of the characteristic fields, which should scale with the strengths of the chiral Dzyaloshinskii-Moriay coupling, from the usual properties of chiral cubic helimagnets. The temperature-dependence of the ferromagnetic saturation field $H_{c2}(T)$ is anomalous, in correspondence to a strong temperature dependence of the magnetic modulation length in the range 3 to 9 nm observed by small-angle neutron scattering experiments on polycrystals [11, 12]. An anomalous Hall effect contribution found by electrical transport measurements in polycrystalline bulk samples of MnGe at low temperatures [11] has been interpreted as indication of a complex spin texture such as a Skyrmion lattice, earlier predicted to exist in chiral ferromagnets [13, 14].

Further investigations on the basic magnetic properties of this compound are desirable to understand the origin of the anomalous magnetic phase diagram and transport data. Here, results from density-functional theory (DFT) calculations are reported on the magnetic properties of MnGe. The theoretical results allow to predict an interesting evolution of the basically ferromagnetic properties in this compound under pressure.

2. Method

Calculation have been performed using a full-potential local orbital method, as implemented in the FPLO code [15], with the generalized gradient approximation (GGA) parametrized by Perdew, Burke Ernzerhof[16]. For comparison also the local spin-density approximation (LSDA) from Perdew and Wang [17] has been used. In the calculations energies have been converged to better than $10^{-8}$ Ha / unit cell, and electron densities to better than $10^{-6}$ electrons/(a.u.)$^3$. Different magnetic states are found by the DFT calculations. Searches for these co-existing spin states have been done by fixed spin-calculations at various reduced lattice parameters compared to the experimentally reported $a = 4.795$ Å at RT [10]. Structure optimization of the B20 cells was performed for all calculated volumes and the different magnetic states with forces on the ions reduced to less than $10^{-3}$ eV/Å using the scalar relativistic option in the FPLO code. Reported results pertain to these calculations with the GGA, if not stated otherwise.

3. Results

The search for different magnetic states in MnGe resulted in the observation of a ferromagnetic high-spin (HS) state and a low-spin (LS) state with a spin-moment of only 1$\mu_B$/ f.u. In the calculation using GGA, the HS state with a moment slightly larger than 2$\mu_B$/ f.u. forms the energy minimum at zero pressure. For the LSDA, the LS state is the global minimum. Comparison with the experimental saturation magnetization suggests that the GGA provides the better theoretical description of magnetic properties in MnGe. The DFT results, as depicted in Fig. 1, also show that (i) the HS state is destabilized by reducing the volume of the unit cell, i.e. applying pressure; (ii) the existence range for the LS state is restricted to a certain range of lattice parameters; (iii) for low volumes the magnetic moment in the LS state is reduced, and (iv) this state finally collapses into a non-magnetic zero-spin (OS) state without spin splitting of the electronic bands. The dependence of the total energy on lattice parameter, Fig. 2, has been fitted by the Murnaghan formula to derive the equation of states (eos) for the three different magnetic states, the results are collected in Table 1.

The evolution of the band-structure is shown by the (spin-split) density of states (DOS) in different magnetic states in Fig. 3. The LS structure is half-metallic with a narrow gap in the bands for majority spin at the Fermi edge. For reduced lattice parameter a metallic state is
Figure 1. Magnetic moment vs lattice parameter for the three different magnetic states.

Figure 2. Total energy vs lattice parameter for the three different magnetic states. Symbols are results from the DFT calculations. Lines are fits to the Murnaghan formula.

Figure 3. Density of states (DOS) with decreasing lattice constant: \( a = 4.769 \) Å in HS state close to equilibrium lattice constant at ambient pressure. \( a = 4.600 \) Å half-metallic LS state under pressure. \( a = 4.400 \) Å metallic LS state under higher pressure. \( a = 4.200 \) Å non-spin polarized 0S state at highest pressure.

Found, as the majority spin DOS shifts upwards in energy. The LS state finally collapses and the spin-splitting of the band-structure is lost. From the eos results, the pressures for the various transitions can be estimated. The first-order transition from HS to LS state is expected at about 18 GPa, the metallic LS state sets in around 40 GPa, and the pressure collapse of the magnetic moment should occur as a first-order transition between LS and 0S state at or above 75 GPa.

The transition pressures are estimates with relatively large uncertainty. This uncertainty is apparent already from the stabilization of the LS state in the LSDA calculations for ambient pressure.

4. Conclusions
The theoretical results suggest that MnGe would allow to investigate the effects of complex spin-textures on the transport in a half-metallic state, i.e. with only one spin character of the electrons at the Fermi edge. The half-metallic LS state should be realizable in experiments.
Table 1. Results of the total energy calculations for the different spin states. Using GGA [16] and LSDA [17] functional. Average spin \( < s > \) is quoted for the reachable state with lowest energy at lattice parameter \( a \). Remaining columns are parameters from the Murnaghan fits: the equilibrium volume \( V_0 \) per atom, \( \Delta E \) the total energy at this volume with respect to global energy minimum, and \( B_0, B'_0 \) bulk modulus and its pressure derivative. Note, the LS state in GGA and the HS state in LSDA, the corresponding equilibrium states are not reachable in the calculations. The experimental lattice constant is \( a = 4.795 \) Å at RT [10]. Arras et al. have calculated \( a = 4.80 \) Å in a GGA-DFT study [6].

|        | \( a \) [Å] | \( < s > \) [\( \mu B \)/f.u.] | \( V_0 \) [Å³/atom] | \( \Delta E \) [meV/f.u.] | \( B_0 \) [GPa] | \( B'_0 \) |
|--------|-------------|-------------------------------|-------------------|---------------------|----------------|-------------|
| GGA:   |             |                               |                   |                     |                |             |
| HS     | 4.77        | 2.01                          | 13.56             | 0                   | 136            | 5.0         |
| LS     | 4.67        | 1.00                          | 12.99             | 77.4                | 187            | 3.6         |
| 0S     | 4.70        | 0                             | 12.89             | 179.8               | 176            | 4.3         |
| LSDA:  |             |                               |                   |                     |                |             |
| HS     | 4.67        | 1.24                          | 12.33             | 19.6                | 147            | 3.45        |
| LS     | 4.60        | 1.00                          | 12.19             | 0                   | 201            | 4.0         |
| 0S     | 4.58        | 0                             | 12.06             | 40.27               | 213            | 4.2         |

with standard high-pressure devices. It is also conceivable to shift the narrow band gap in the majority-spin bands through the Fermi edge by strains in epitaxial films.

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