

Predicting Half Metallic Ferromagnets – A Little Bit More Realism Please

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In this paper we critically examine recent claims about half metallic ferromagnetism in open p-shell systems. Odd valence electron compounds like CaAs have been predicted to show a 100 % spin polarization at the Fermi level, if they can be grown in the zincblende structure. It has furthermore been argued that this should be possible under special conditions. We will give several arguments against this claim based on concepts from chemistry and density functional calculations.

1 Introduction

Ever since half metallic ferromagnets (HMFs) have been theoretically discovered by de Groot^[1] in the half Heusler compound MnNiSb, HMFs have been a widely studied topic in condensed matter physics and material sciences. A HMF is a ferromagnet with an extremely high spin polarization^[2] and can occur in many structure types such as Heusler compounds, perovskites and other transition metal oxides such as CrO₂. One of the unique features of a HMF is a 100 % spin polarization at the Fermi level, making HMFs ideal candidates for spintronic devices, e.g. in combination with MgO tunnel junctions. Semiconducting relatives are the precondition for half metallic ferromagnetism because a gap in one spin direction is necessary to achieve the desired 100 % spin polarization.^[3] The underlying physical mechanism for this effect is large intra-atomic exchange in some magnetic Heusler compounds, leading to an electronic structure sketched in Fig. 1a). Manganese for example acquires a large magnetic moment in an octahedral environment and carries a formal d⁴ configuration which has been explained by Kübler and coworkers.^[4] The magnetic moment is in agreement with the Slater-Pauling rule, which allows the prediction of new HMFs by simply counting the valence electrons.^[3] Half metallic ferromagnets with a high curie temperature would have a huge impact on spintronics, but up to now only some Heusler compounds come near to the desired performance.

Basically all HMFs are based on transition metal d-shell compounds, but recently more and more people have started to investigate p-shell magnetism in odd electron compounds such as CaAs in the zincblende and other simple binary structures such as the rock salt (NaCl) or wurtzite structure, which are not the thermodynamically stable structures. The general claim is that it should be possible to stabilize compounds such as CaAs in those structures as metastable materials under certain conditions. Open p-shell systems are known as radicals in chemistry, which usually are not stable, with some exceptions such as in extended π -electron systems. What they find are compounds that show half metallic ferromagnetism, if they crystallized in structures with tetrahedral coordination (see Ref. [5] and references

therein).

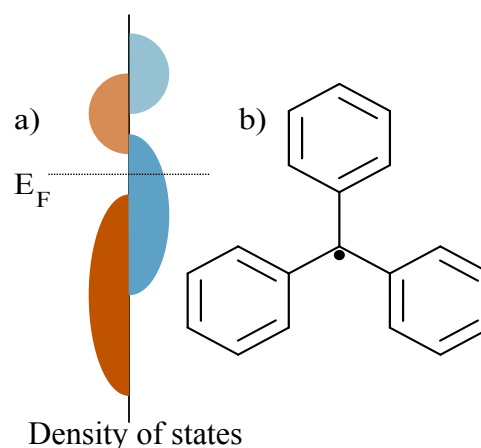


Figure 1: **a)** Schematic DOS of a HMF. **b)** Triphenylmethyl radical.

2 Outline

In this letter we want to question the feasibility of p-shell magnetism of binary compounds in zincblende structures, especially the existence of metastable systems. We will discuss our thoughts on this topic by choosing CaAs as an example, because here the actual occurring crystal structure is well known. This letter does not claim to be a complete treatise on the topic (a more sophisticated analysis will be published elsewhere). We rather want to introduce the reader to our arguments based on chemical intuition supported by density-functional theory (DFT) calculations. It is important to stress that the mere purpose of our calculations in this paper is just to illustrate ideas. They should not be taken as a proof that the claims are wrong. Rather, they are just a hint that much more work with more sophisticated methods lies ahead. To really determine if a structure is thermodynamically stable with respect to another phase, molecular dynamics calculations have to be performed.

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3 Discussion

CaAs crystallizes in a layered hexagonal structure. The layers consist of buckled CaAs hexagons resembling a structure related to cyclohexane. Another striking feature is the existence of As₂ dimers at the edges of the unit cell, as can be seen in Fig. 2d). CaAs can be understood in the context of Zintl compounds. In general, stable compounds tend to have a formal closed shell configuration, which can be accomplished by different types of bonding in solid state compounds, alternatively metals are formed. We will now argue against these claims and show that the half metallic ferromagnetic structures should be unstable with respect to the naturally occurring structure using ideas from chemistry and DFT calculations.

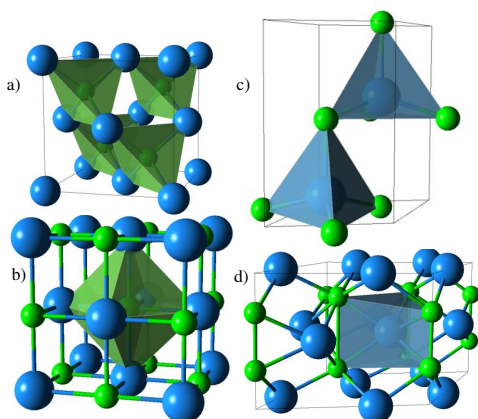


Figure 2: Unit cells of a) zincblende, b) NaCl, c) wurtzite, and d) the real hexagonal structure. Notice the different types of coordination.

CaAs is a 7 valence electron compound. Because of the difference in electronegativity of Ca and As, we could think of this compound as consisting of Ca²⁺ and As²⁻. In this configuration, As²⁻ has a single unpaired electron and can be described as a radical which would contribute to paramagnetic behavior.

In chemistry, radicals are usually not considered to be stable, i.e. there will be many side reactions that will destroy the radical state, e.g., reaction with O₂. Despite this, we know several circumstances in which stable radicals exist.

- Magnetic compounds, such as in d- or f-electron systems.
- Delocalization of the radical, as known from aromatic organic molecules such as the triphenylmethyl radical in Fig. 1b).
- Kinetic stabilization, i.e. steric effects prevent the radical from reacting with other molecules.²

How can we achieve such a stabilization in our solid state problem? Delocalization occurs when conjugated π -orbitals overlap and thus the Hamiltonian matrix elements

should be large. Since the hopping parameter t within the tight-binding approximation is proportional to these matrix elements, while the bandwidth is proportional to t , we would expect to see a large bandwidth in the band structure for the radical state of As, indicating delocalization. Another possibility is the formation of a covalent bond between two radical partners resulting in a closed shell electronic structure. These things are well known to chemists and rely on very simple but accurate concepts such as the Zintl concept. A stable structure should now either show a large bandwidth of the valence band or should have As-As bonding interaction within its structure.

All calculations have been performed with the WIEN2k code using the PBE-GGA functional.^[6] The lattice constants have been relaxed, as well as the internal coordinates of single atoms, if not constrained by symmetry. We calculated total energies, the density of states for both spin channels as well as a spin polarized band structure for CaAs in hypothetical zincblende, wurtzite and NaCl structure and compared them to the electronic structure of the real compound. The plane wave cut-off parameter $R_{MT}K_{MAX}$ was set to 7 and the Brillouin zone was sampled by 4000 k-points. It turns out that the buckled hexagonal structure with the dimers is much lower in energy per formula unit compared to all other structures (Tab. 1). In zincblende and wurtzite structures, tetrahedral sp^3 bonding plays the most important role and interestingly half metallic ferromagnetism exists in this structures. The band structure for the zincblende calculations shows the typical gap in the minority spin channel and a constant shift of energy for the majority spin channel. Taking a look at the density of states we can immediately see the occupation difference of both spin directions, leading to a magnetic moment of 1 μ_b per unit cell for both tetrahedral structures. The small differences in the density of states can be attributed to the lower symmetry in the wurtzite structure compared to the zincblende compound. Coming back to our previous considerations, we can neither find a large bandwidth in the valence band, nor covalent As-As bonds in these structures. On the contrary, the bandwidth for the valence band (the radical band) in the zincblende structure is very small (0.16 eV), which can be attributed to a very localized state.

Going away from the tetrahedral structures we find a much lower spin polarization for CaAs in the NaCl structure, which can be attributed to the higher octahedral symmetry and coordination number. A very interesting fact is the high polarization of the low lying s bands, which is in agreement with non-directed bonding. The band structure shows a large bandwidth (1.9 eV) of the valence band, which explains the much smaller energy difference to the experimentally observed structure. One reason for the non-realization of the NaCl structure must be traced back to the fact that a bonding As-As interaction is not present in this structure, because of the high coordination number, which does not favor covalent bonding in contrast to ionic interactions.

²Even under ultra high vacuum conditions, many organic radicals still react with remaining traces of hydrogen (or other molecules) in their environment resulting in lifetimes in the order of milliseconds if not stabilized by kinetic control.

Table 1: Energies per formula unit (FU) for CaAs in different structures.

Structure	E_{FU} / Ry	$E_{FU}^{\text{struc}} - E_{FU}^{\text{real}} / \text{kJ mol}^{-1}$
Zinblende	-5883.031913	148.0
Wurtzite	-5883.038164	139.8
NaCl	-5883.097351	62.1
Real structure	-5883.144661	0

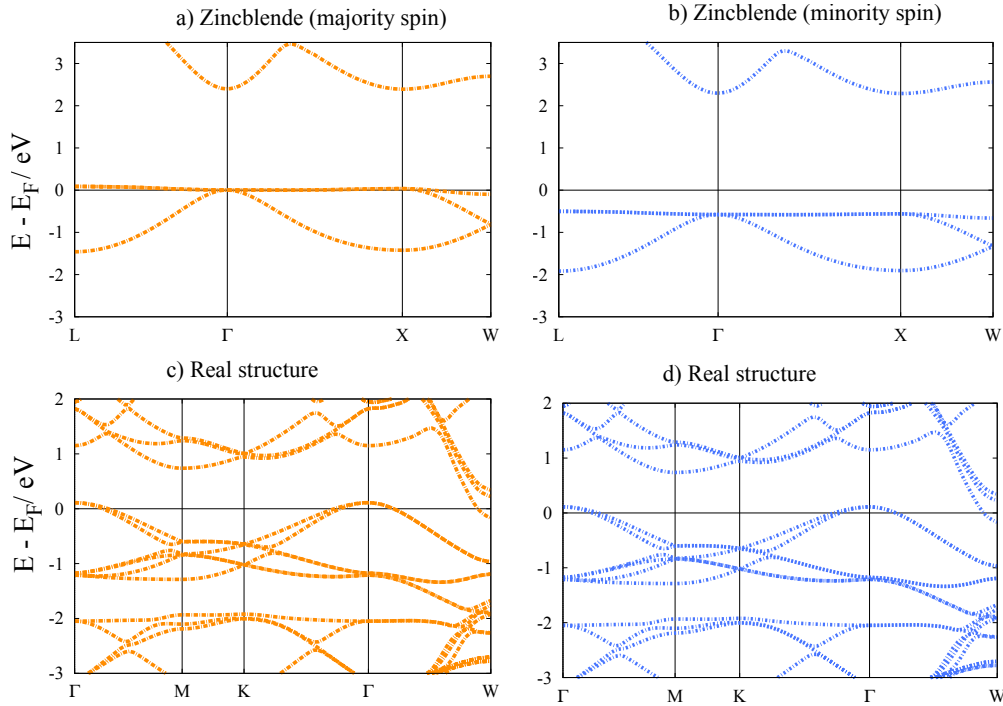


Figure 3: Band structures of CaAs in zincblende, and in the real structure.

In the real structure now both ways of stabilizing the radical character of this compound are present. Not only do we have dispersive bands at the Fermi level, but we can also observe As_2 dimers within the structure and due to the lower symmetry, two crystallographically different As positions exist in this structure, which can be seen in the tilt of the trigonal prism as shown in Fig. 2d).

A further indicator for this stability can be found in the density of states (DOS), since the DOS of the stable structure shows a minimum at the Fermi level, to which in contrast all other structures show a maximum, indicating an electronic destabilization of the structures.

Next to this very basic discussion, further remarks on the level of theory have to be pointed out. Usually, localized states are not treated correctly within LDA/GGA calculations and related methods, so more correlation effects have to be taken into account, which for instance can be observed

in Rb_4O_6 .^[7] In this compound, open shell hyperoxide O_2^- anions coexist with O_2^{2-} peroxide anions, the former having an unpaired electron. Regular methods such as LDA predict a metallic ground state. Only more sophisticated methods such as hybrid functionals yield a magnetically frustrated ground state in agreement with experiment, which shows the importance of electronic correlation in open p-shell systems. Returning back to our simple example, this observation has an important consequence, since all calculations so far have been performed with methods that do not treat correlation effects very well and might give the wrong ground state. Thus, in order to verify that the predicted compounds really show the desired property, a careful investigation of all possible structures and magnetic configurations together with more exact methods is mandatory as already mentioned in the outline.

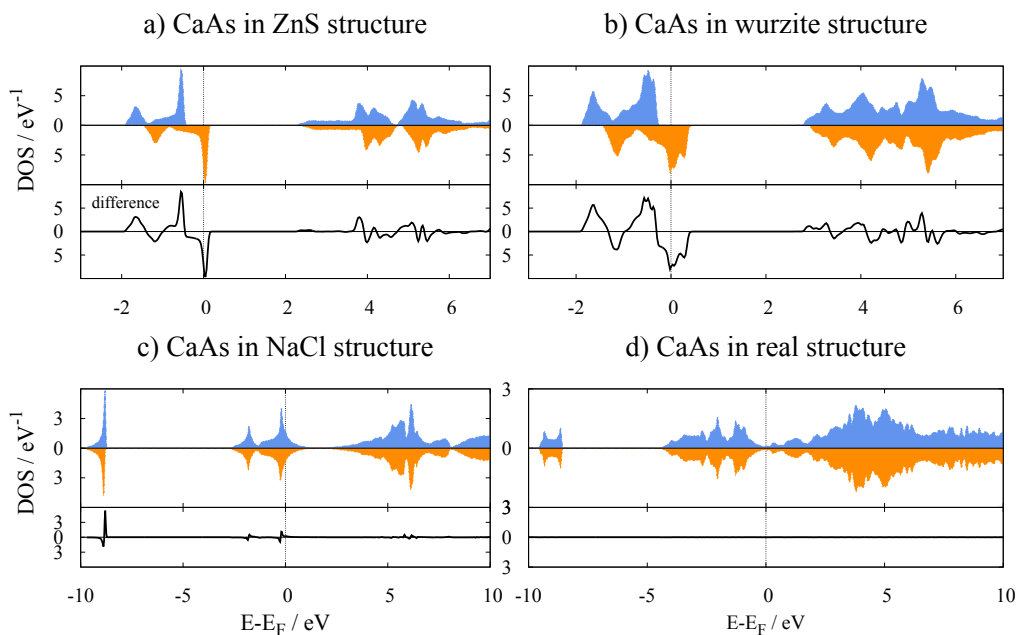


Figure 4: Density of states per formula unit for CaAs in zincblende, wurzite, NaCl, and the actually occurring structure.

4 Summary and Conclusions

We will now quickly summarize our observations:

- Radicals are usually not stable with respect to further side reactions, if not stabilized by kinetic control or delocalization.
- Hallmarks of such stabilization could be dispersive bands with a large bandwidth at the Fermi level, but none of the proposed alternative structures shows this, except for the NaCl structure.
- Arguing with the Zintl concept, one would also expect the formation of dimers within a stable structure, which only occurs in the real structure.
- Inclusion of correlation effects will most likely result in a different ground state (see Rb_4O_6).

We hope we could convince the reader that chemical intuition can help to identify unrealistic predictions with the support of computational methods. Despite the interesting emergence of magnetism in tetrahedral structures, such claims should only be made with emphasis on the theoretical implications (i.e. the mechanism). Actually claiming that unrealistic structures can eventually be grown is not only wrong, but will also cause confusion within the community. There is nothing wrong with calculating things that do not exist (this is what theory is for), but it should always be pointed out very clearly.

Without a careful optimization of the structure and taking into account electron correlation, a naive scientist could thus predict an endless number of new half metallic ferromagnets, just by combining elements with an odd number of electrons per unit cell.

In conclusion and in the spirit of Roald Hoffmann's paper on the prediction of new molecules,^[8] we thus demand more care and realism when predicting new materials. Please!

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