Ferromagnetism in Tetrahedrally Coordinated Compounds of I/II-V Elements: *Ab Initio* Calculations

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INTRODUCTION

Recently Kusakabe et al. [1] proposed magnetic zinc-blende CaAs as a possible material for spintronics application. Their proposal was motivated by the need for half metallic ferromagnets (HMF) in spintronic devices [2], which are seen as key ingredients. However, apart from the technological application the magnetic I/II-V compounds represent a new class of ferromagnetic materials where magnetic order is carried by the anion p-electrons without any direct involvement of d-electrons as in the magnetic transition metals and their compounds. The p-electron magnetism in CaAs and the other I/II-V systems appears in the fully ordered stoichiometric compounds and their magnetic order is intrinsic and not triggered by the presence of crystal defects of various kinds.

TOTAL ENERGY

By applying density functional theory (DFT) within the generalized gradient approximation of Perdew, Burke and Ernzerhof [3] using the FLAIR [4] code, an implementation of the full potential linearized augmented plane wave method (FLAPW) [5], we rst investigated the stability of CaAs, the prototype of the so-called half-metallic-ferromagnets (HMF) of this type. In Fig. 1 the total energy is plotted over the volume per formula unit for various crystal structures including zinc-blende (ZB), wurtzite (WZ), sodium chloride (NaCl) and the experimentally found structure NaO (P62m). Our calculated lattice constants for the true ground state (NaO) with a=15.03 bohr and a/c=1.326 (xed) are in good agreement with the experimental values of a=14.84(2) and c=11.19 [6]. Furthermore we found out that the ground state of CaAs found experimentally is energetically rather far away from the structures which are expected to exhibit HMF ($\approx$ 1.4 eV/f.u.). However, since e.g. CrAs and CrSb have already been prepared successfully in the ZB structure even though it is not their equilibrium crystal structure, also for CaAs a preparation as a thin lm on a substrate may be possible.

ELECTRONIC PROPERTIES

All ZB compounds composed of group I/II elements as cations and group V elements as anions investigated combine two key features, namely a relatively wide band-gap of approximately 2 eV present in both spin channels (in an LSDA approximation), and a ferromagnetic ground state with an integer magnetic moment obeying a simple $|8 - n|$ rule, n being the total number of valence electrons. The large difference in electronegativity between the constituent elements leeds to a charge transfer causing a gap between occupied bands having predominantly p-character and empty bands with s and/or d character. The band structure for CaAs as one representative is plotted in Fig. 2, most interesting is the uppermost occupied band being almost dispersionless. This at ness is caused - amongst others - by the relatively large lattice constant of these compounds (between 9.15 bohr for MgN and 15.37 bohr for BaSb). For the representatives having cations with empty d-bands in the energetic proximity of the Fermi energy (e.g. Ca, Sr, Ba), additionally a curious anion-p – cation-d hybridization occurs, which further reduces the dispersion of the so-called at band.

All compounds investigated exhibit a well localized

magnetic moment proportional to the number of holes in the almost atomiclike anion p-band. A systematic study of these compounds showed that the origin of this p-electron magnetism can be understood in terms of the Stoner-criterion, which predicts instabilities towards magnetism due to the high density of states at the Fermi energy in the hypothetical nonmagnetic state caused by the at band.

Comparisons of the total energy between a ferromagnetic (FM) and an antiferromagnetic (AFM) ground state - including augmented spherical wave (ASW) [7] calculations that allow for the set up of so-called spin-spirals - in all cases showed relatively large energy gains (between 50 meV and 220 meV) for the system to adopt the FM ground state (see Fig. 3). In a mean el d approximation also the paramagnetic Curie temperature has been estimated, resulting in a value of 680 K for CaAs, which would be well suited for technological application.

CONCLUSION

We nd that half metalicity is very common among ionic compounds composed of alkaline earth/alkali metals and group V elements if a tetrahedrally coordinated crystal structure like the ZB or WZ structure is assumed. Despite the fact that CaAs exists as bulk phase at best in metastable form, however, its highly interesting magnetic properties including p-electron magnetism, the occurrance of an extremely at band being of interest in the context of the Hubbard model, and a reasonably high Curie temperature will warrant also experimental efforts to stabilize these materials in a fourfold coordinated structure such as ZB or WZ (e.g. via vacuum laser deposition) on suitable substrates.

REFERENCES

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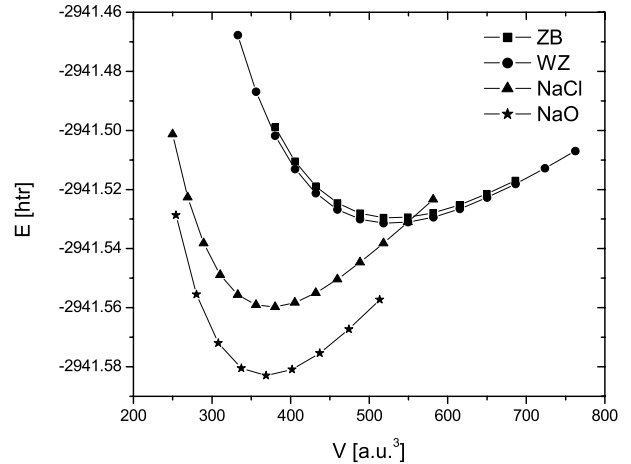[7] A. R. Williams, J. Kübler, and C. D. Gelatt Jr., Phys. Rev. B **19**, 6094, (1979).

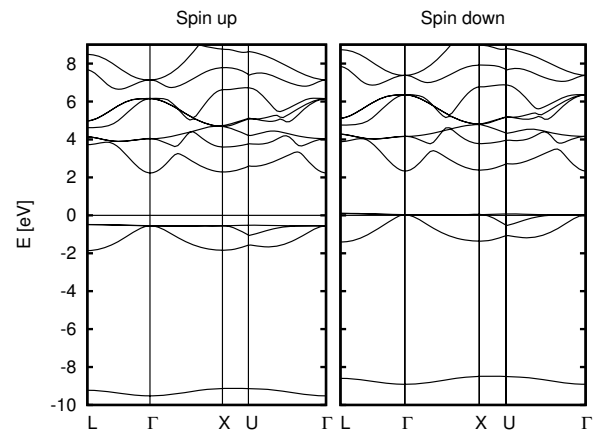Fig. 1. Total energy for CaAs in different crystal structures. Energies and volumes are given per formula unit.

Fig. 2. Band structure of ZB-CaAs for both spin channels. A half lled, extremely at band is present at the Fermi energy.
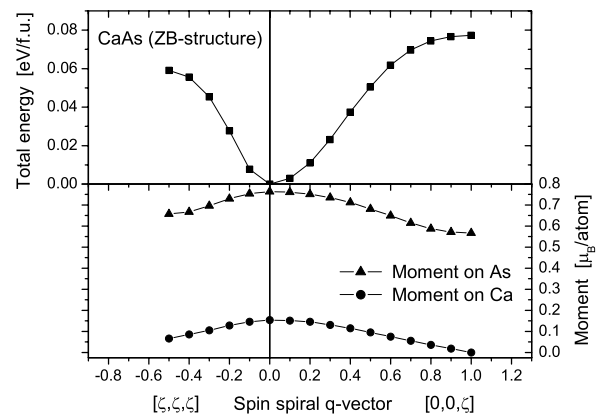

Fig. 3. Upper panel: total energy as a function of the spin spiral in $[\zeta,\zeta,\zeta]$ and $[0,0,\zeta]$ direction, respectively. The spin spiral propagation vector **q** is given in multiples of $2\pi/a$. Lower panel: magnetic moment of Ca and As.