Hessisches Kompetenzzentrum
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# *Rational Design of Narrow-Hysteresis Materials by Tailoring Magnetoelastic Interactions III*

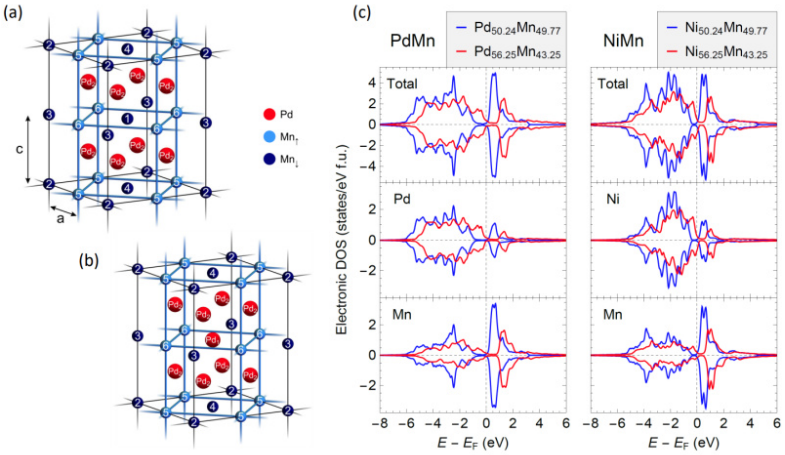


Figure 1: (a) Equiatomic PdMn and (b) the structure where the Mn atom in the center is replaced by a Pd atom (Pd1). This leads to the emergence of a nonzero net magnetic moment. The two AFM sublattices of the Mn atoms are indicated by two different shades of blue. Supercells for the first-principles calculations are formed by a 3×3×3 elongation of the 16-atom cell. (c) Total (first row) and element-resolved (second and third rows for Pd/Ni and Mn, correspondingly) electronic DOS of PdMn (left panel) and NiMn (right panel). Passing from smaller (blue curves) to larger (red curves) Pd/Ni-excess content, increasing of valence electron concentration results in shifting of the whole DOS weight towards higher energies pushing the pseudo-gap above the Fermi level. Figures from Phys. Rev. B 108, 064417 (2023). Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license.

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Clusters
Lichtenberg II Cluster Darmstadt

Software
VASP

Additional Software
Phonopy

Institute
Center for Nanointegration

University
Universität Duisburg Essen



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## Introduction

Functional materials for magnetic cooling devices at room temperature are in focus for the materials scientists during several decades. Magnetic cooling technology based on magnetocaloric effect (MCE) is considered as alternative to conventional gas refrigeration due to its high efficiency and environmental friendliness. By successively applying or removing an external magnetic field to the magnetic material at a phase transition, the MCE enables effective heat transmission. A material suitable for magnetic refrigeration should exhibit substantial variations in entropy and temperature in repeated magnetic field cycles as well as a narrow hysteresis. Theoretical investigation in the framework of density functional theory (DFT) is extremely helpful since it allows for an effective and reliable prediction of intrinsic material properties at the nanoscale without experimental input. Our goal within this project is to identify the complete set of relevant microscopic mechanisms, which link the structural, electronic, and magnetic degrees of freedom in functional materials, and predict state-of-the-art multifunctional alloys that exhibit exceptional magnetocaloric properties and are promising for application in the magnetic cooling devices.

## Methods

We employed DFT as implemented in the Vienna ab initio simulation package (VASP), to characterize the structural, electronic, magnetic, and vibrational properties of the materials at the nanoscale. VASP allows for modeling of large systems on super-computer hardware, which is crucial for phonon computations. The wavefunctions of the valence electrons are described by VASP using a plane-wave basis set, and the interaction with the core electrons is handled using the Projector Augmented-Wave (PAW) approach. Exchange-correlation energy was treated in the framework of the semi-local generalized gradient approximation, which depends on the local electron density and its gradients, in the Perdew-Burke-Ernzerhof (PBE) formulation. The direct (force-constant) method was used for the phonon calculations. Hellmann-Feynman forces were computed using VASP, while Phonopy was employed for postprocessing and atomic displacement selection.

## Results

During last year, we continued with the modeling of the energy phase diagram for Ni-Mn-based Heusler alloys including all-*d*-metal series Ni-Co-Mn-Ti. The special attention was paid to twinning structures and positional disorder in these materials. In the framework of collaboration within CRC/TRR 270, we also performed large-scale modelling for PdMn (NiMn) with excess Pd(Ni). Our colleagues found from the experiment that annealing PdMn with excess Pd in a magnetic field leads to strongly pinned uncompensated magnetic moments. Large-scale DFT calculations conducted on Lichtenberg II showed that the replacement of one Mn atom by Pd in equiatomic antiferromagnetic (AFM) PdMn changes the magnetization

significantly in the vicinity of this defect. The excess Pd atom itself acquires a moment of 0.347 $\mu_B$ oriented parallel to the magnetic moments of the closest Mn atoms in the plane. The eight regular Pd atoms surrounding the defect also acquire small magnetic moments (0.030 $\mu_B$). As a result, the layered AFM configuration is no longer compensated, and the structure as a whole has a net moment above zero. Thus, one Pd substitution generates, also including the polarization cloud involving the nearest Pd neighbors, a total magnetic moment of 4.977 $\mu_B$, which is slightly smaller compared to a Ni-excess atom in NiMn. The results of this work are published in Phys. Rev. B 108, 064417 (2023).

## Discussion

Of particular interest was how further increasing in defect concentration would affect the electronic structure of PdMn. Therefore, we additionally performed the full relaxation of a system with 6.25 at.% Pd excess. Counterintuitively, the changes cannot simply be described by the rigid band model, where the additional *d*-electrons shift the Fermi level $E_F$ and increasing Pd-excess would be expected to shift the Fermi level into the larger peak above the pseudogap. However, the calculation shows that weight from the unoccupied densities of states (DOS) is redistributed below the pseudogap, and $E_F$ finally locates at the bottom edge of the gap. As a consequence, the occupied 3*d* states move in total closer to the Fermi level, which is associated with an increase in band energy. We speculate that this suppresses clustering of the excess Pd when the overall Pd concentration is low enough to keep $E_F$ close to the upper edge of pseudogap and, therefore, supports the field-induced diffusion of the excess-Pd atoms. The situation is similar to NiMn, where the pseudogap is, however, two times smaller.

## Publications

Josten, N.; Miroshkina, O.; Acet, M.; Gruner, M.E.; Farle, M.: "Annealing time, temperature, and field dependence of pinned magnetic moments in the collinear antiferromagnet PdMn", Physical Review B 108, 064417 (2023). https://doi.org/10.1103/PhysRevB.108.064417">https://doi.org/10.1103/PhysRevB.108.064417

Markus Gruner, International Conference on Ferromagnetic Shape Memory Alloys (ICFSMA), College Station (Texas), USA, 14 – 19 May, 2023.

Olga Miroshkina, DPG Spring Meeting of the Condensed Matter Section (SKM), Dresden, Germany, 26 - 31 March, 2023.

Olga Miroshkina, Joint European Magnetic Symposia (JEMS), Madrid, Spain, 27 August - 1 September, 2023.

Olga Miroshkina, IEEE Around-the-Clock Around-the-Globe Magnetics Conference (AtC-AtG), online worldwide, 27 September, 2023.

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