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Mixing thermodynamics of $TM_{1-x}Gd_xN$ (TM=Ti,Zr,Hf) from first principles

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The mixing thermodynamics of GdN with TiN, ZrN, and HfN is studied using first-principles methods. We find that while $Ti_{1-x}Gd_xN$ has a strong preference for phase separation due to the large lattice mismatch, $Zr_{1-x}Gd_xN$ and $Hf_{1-x}Gd_xN$ readily mix, possibly in the form of ordered compounds. In particular, $ZrGdN_2$ is predicted to order in a rocksalt counterpart to the $L1_1$ structure at temperatures below 1020 K. These mixed nitrides are promising candidates as neutron absorbing, thermally and chemically stable, thin film materials. © *2011 American Institute of Physics*.
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Gadolinium has the highest thermal neutron absorption of all elements. The cross-section for the nuclear reaction, σ, is 49 700 b for natural Gd and as high as σ=259 000 b for pure ^{157}Gd, which is a nonradioactive stable isotope with a natural abundance of 15.65%. Thus, the development of Gd-containing materials is of high interest for many technical applications of neutron radiation. For instance, Gd has been suggested as a key component in new generations of neutron detectors.[1,2] Such devices are highly needed due to the upcoming ^{3}He shortage crisis[3] in conjunction with a rising demand in security controls to prevent smuggling of fissile materials as well as in new large scale neutron scattering facilities.[4] Gd compounds also have a potential for usage as pure absorbers to prevent cross-talk between detector segments and thus improving the detector resolution. Furthermore, it can be used in capture agents in medical thermal neutron therapy[5,6] and it is an extremely efficient shielding material for thermal neutron radiation protection. Those diverse applications naturally apply a range of different constraints, in terms of chemical, mechanical, and thermal stability of the materials, as well as demands on electrical conductivity, and underlines the importance of a broad research on Gd-containing materials systems.

Nitrides are a materials class that have proven extremely useful in a large number of technological applications, including wear resistant coatings[7,8] and diffusion barriers.[9] One important reason is their straight forward application, using physical or chemical vapor deposition (PVD/CVD) techniques, on the most varying types of surfaces. GdN, crystallizing in the cubic rocksalt structure[10] and being possible to grow with PVD (Ref. 11) and CVD,[12] could thus be considered as a means for applying Gd-containing thin films for neutron detection or absorbing purposes. In fact, GdN with a cubic lattice parameter of ~5.00 Å (Refs. 10 and 13) has a higher Gd-content per unit volume than Gd_2O_3 (Ref. 14) and even pure Gd metal. Unfortunately, pure GdN shows low resistance against oxidation[13,15] and its mechanical and thermal stability is not well established. One approach to utilize GdN under demanding environmental conditions is to provide a protective layer of a more chemically, mechanically, and/or thermally stable nitride. Another approach could be to alloy GdN into a matrix of such a nitride. These methods can also be used to obtain neutron absorbing films that are good electrical conductors needed to avoid charge buildup at absorbing separation films inside detectors.

Growing multicomponent nitride films are standard procedure today but for both strategies, the knowledge of the mixing thermodynamics of the constituent nitrides is of importance. In this work, we report the results of a theoretical study of the mixing thermodynamics of GdN with the thoroughly studied, hard, chemically quite inert, thermally stable, and electrically conductive transition metal nitrides TiN, ZrN, and HfN.

Our calculations are based on density functional theory calculations using the projector augmented wave method[16] as implemented in the Vienna *ab initio* simulation package (VASP).[17] The electronic exchange-correlation effects are modeled using a combination of the generalized gradient approximation[18] with a Hubbard Coulomb term.[19] The U-term is applied only to the 4f-shell of Gd and its effective value $(U-J)$ is chosen to 8 eV as suggested in Ref. 20. Due to the half-filled character and corresponding strong spin-splitting of this band, the exact value of this parameter has very little influence on the properties studied in this work. All calculations are done in a ferromagnetic configuration of the Gd-spin moments. No significant differences in mixing energetics were found when we tested to distribute the magnetic moments of Gd in a disordered manner.[21] This was the case even though this paramagneticlike state of GdN was found to be semiconducting rather than barely a semimetal as in the ferromagnetic calculation.

The substitutionally disordered solid solutions of $TM_{1-x}Gd_xN$ are modeled using special quasirandom structures (SQSs) (Ref. 22) with the compositions x=0.125, 0.25, 0.325, 0.50, 0.625, 0.75, and 0.875. To obtain equilibrium volumes the SQSs suggested in Ref. 23 are used. To obtain converged total energies, larger 128 atoms cells are used with pair correlation functions being identical to the ideal disordered case on the first two shells and differing with less than 4% on the first seven shells for all studied compositions. To investigate the ordering tendency in the $Zr_{1-x}Gd_xN$ system we use a concentration and volume dependent cluster expansion (CE) (Ref. 24) of the configurational energy for the treated compositions. As a starting input, the energies of

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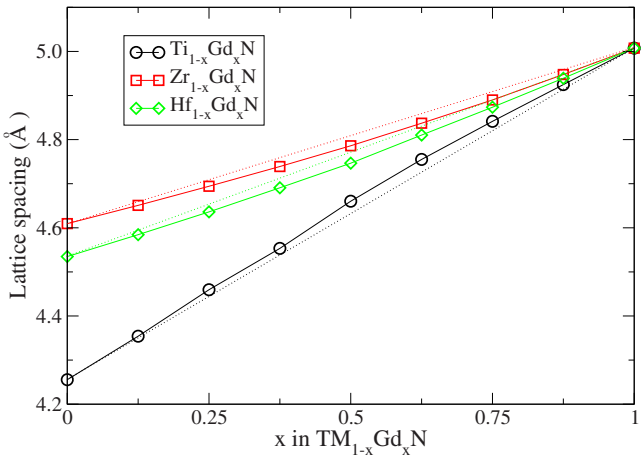

FIG. 1. (Color online) Calculated equilibrium lattice spacing for $Ti_{1-x}Gd_xN$, $Zr_{1-x}Gd_xN$, and $Hf_{1-x}Gd_xN$ solid solutions as a function of GdN content. The dotted lines indicate Vegard's rule.

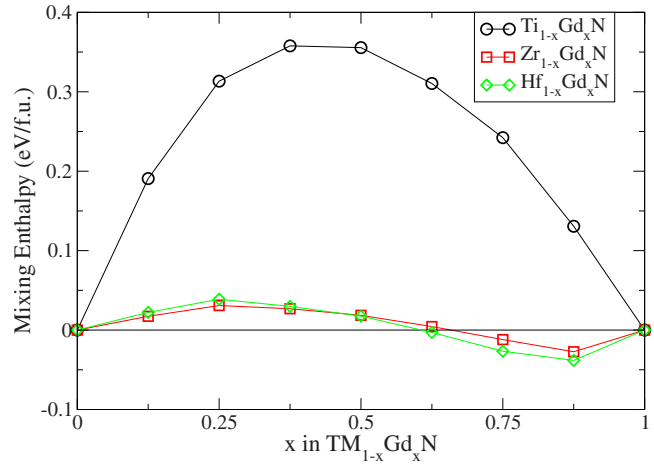

FIG. 2. (Color online) Calculated mixing enthalpies of substitutionally disordered solid solutions of $Ti_{1-x}Gd_xN$, $Zr_{1-x}Gd_xN$, and $Hf_{1-x}Gd_xN$ as a function of GdN content.

20 different ordered compounds are calculated from first principles for each composition at the volumes obtained for the SQSs. Then a least-square procedure is used to map their mixing energies onto the first ten pair clusters of a generalized Ising Hamiltonian. In a refinement step, these interactions are used to find low-energy structures by a ground state search of the configurations in a few 16 and 24 atoms supercells. The energies of the identified structures are then evaluated with first-principles calculations and included in the CE now extended to 13 pair clusters. In a final step, the obtained effective cluster interactions are used in a simulated annealing Monte Carlo study to identify the lowest energy state for each composition.

The calculated equilibrium lattice parameters of the $TM_{1-x}Gd_xN$ solid solutions are shown in Fig. 1. For the binaries the calculated (experimental[25]) values in angstrom are TiN 4.255 (4.24), ZrN 4.61 (4.57–4.58), HfN 4.53 (4.51–4.53), and GdN 5.01 (4.98–5.00). The $Ti_{1-x}Gd_xN$ solutions show a positive deviation from the linear Vegards rule. A positive deviation is qualitatively understandable in cases like the present where the lattice spacings of the constituents are very different. Due to the anharmonicity of the binding energy curve, it is energetically more costly to compress the larger compound than to expand the smaller one.

In contrast, the lattice parameters of the $Zr_{1-x}Gd_xN$ and $Hf_{1-x}Gd_xN$ solid solutions show a negative deviation from Vegard's rule. In those cases where the lattice mismatch between the constituents are smaller, the larger bulk moduli of the lower volume compounds ZrN, 264 GPa, and HfN, 286 GPa, as compared to 148 GPa for GdN, that has the larger volume, is the more important factor. Furthermore, stronger interatomic bonds connected to an ordering tendency to be discussed below decrease the lattice spacing for the intermediate compositions.

The knowledge of lattice parameters of nitride solid solutions, calculated from first principles, has proven valuable in previous experimental studies on phase separating mixed nitrides.[26] The results of Fig. 1 can thus serve as a guide in the interpretation of future experimental studies on these systems.

Figure 2 shows the calculated mixing enthalpies of the $TM_{1-x}Gd_xN$ solid solutions. $Ti_{1-x}Gd_xN$ displays a large positive mixing enthalpy with a maximum value of about 0.36 eV/f.u. indicating an energetic driving force for phase separation. Clearly this is the consequence of the large lattice parameter mismatch of TiN and GdN. As a comparison, in the system $Ti_{1-x}Al_xN$, with a maximum of its mixing enthalpy in the B1 structure calculated to be 0.218 eV/f.u., metastable cubic solid solution can be grown with PVD techniques for compositions $x \leq 0.66$ (Ref. 27) but it is almost completely immiscible at equilibrium conditions even at very high temperatures.[28] Thus, while the possibility to grow metastable $Ti_{1-x}Gd_xN$ solid solutions needs further investigations, it is clear that the two systems will not tend to mix under realistic equilibrium conditions.

The mixing enthalpies of the solid solutions in the $Zr_{1-x}Gd_xN$ and $Hf_{1-x}Gd_xN$ systems on the other hand are much smaller and even negative for the GdN-rich compositions. These results show that ZrN and HfN ought to mix more easily with GdN and the question is under which conditions the solid solutions are thermodynamically stable and under which conditions ordered compounds are formed. In pure GdN there are small induced magnetic moments on N *p*- and Gd *d*-states[29] but we find no significant induced moments on Ti, Zr, or Hf atoms. They are in all our cases smaller then 0.07 μ_B in magnitude.

The result of our study of the ordering trends in $Zr_{1-x}Gd_xN$ is shown in Fig. 3. All plotted values are the results of first-principles calculations. The ordered compounds included in the CE procedure are shown with red circles. The ordered compounds identified in the final step of the ground state search are shown with blue squares. The calculated values for the SQSs, modeling the solid solutions, are shown with black circles. The obtained ground state structures are connected with a black line.

It is clear that $Zr_{1-x}Gd_xN$ is an ordering system with several compounds having negative mixing enthalpies. The largest negative value, −0.059 eV/f.u. is obtained for the composition $x=0.50$ where a $ZrGdN_2$ compound with alternating Zr and Gd planes in the [111]-direction, shown as an inset in Fig. 3, is found to be the ground state structure. This rocksalt counterpart to the $L1_1$ (CuPt) ordering of fcc-structures has previously been found in the $Ti_{1-x}W_xN_y$ system.[30] In our case, the origin of this order is a large positive effective cluster interaction on the second metal-coordination shell favoring pairs of different kinds, together

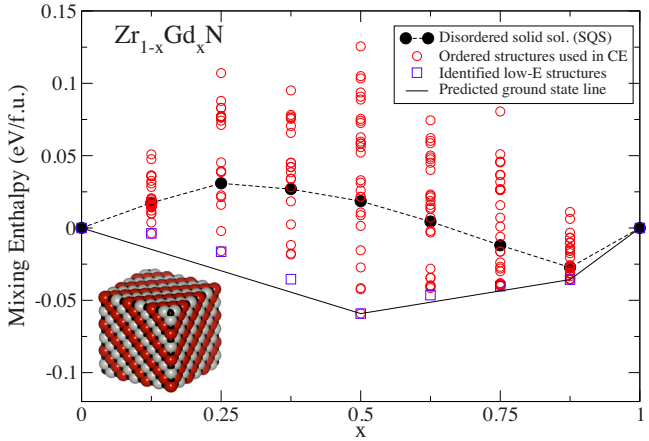

FIG. 3. (Color online) Mixing enthalpies of various phases in the $Zr_{1-x}Gd_xN$ system calculated from first principles. The inset figure illustrates the ordering type observed for the $ZrGdN_2$ compound at $x=0.50$.

with a weak interaction on the nearest-neighbor coordination shell. Order-favoring next-to-nearest metal site interaction was also found in the TiAlN system[23] and concluded to be due to the possibility for nitrogen atoms to relax its bond-lengths when surrounded by different metal type atoms along the ⟨001⟩-directions.

For $x<0.50$ we find no ordered compounds that are energetically stable with respect to pure ZrN and the $ZrGdN_2$ compound. In this composition range the nearest-neighbor cluster interaction turns negative opposing the ordering tendency driven by the second interaction. Our ground state search shows that in this situation the most favorable metal sublattice orderings are combinations of sections with chemically alternating (111)-planes and sections of only Zr planes, although none of them are below the ground state line.

In the GdN-rich regime, $x>0.50$, the situation is more complex. For these compositions we obtain positive values also for the nearest-neighbor interaction and thus a frustrated ordering tendency. For the treated compositions, we find only one additional compound, with the composition $ZrGd_7N_8$, to be a ground state structure. We underline that in the GdN-rich compositions, there could very well exist stable compounds for compositions in between the here treated values but the general trend should be well described by Fig. 3.

Using our effective cluster interactions for the composition $x=0.50$ in a full scale Monte Carlo simulation of the configurational order–disorder transition temperature, we obtain the value $T_c=1020$ K. Since the temperature needed for metal-site diffusion in B1 nitrides is reported to be close to this value,[31] and owing to quantitative uncertainties in our simulations due to neglect of vibrational effects and multisite interactions, experimental investigations are welcomed to probe the possibility of synthesizing the ordered $ZrGdN_2$ compound during growth and during annealing.

In summary, our investigation has revealed that GdN readily mixes with ZrN and HfN while a strong opposition against mixing exists between GdN and TiN due to the large lattice mismatch. Thus, TiN can be used as a stable capping layer on GdN in situations where interdiffusion needs to be minimal also at elevated temperatures. On the other hand, $Zr_{1-x}Gd_xN$ and $Hf_{1-x}Gd_xN$ solid solutions, possibly in combinations with ordered compounds for some compositions, can be a means of applying Gd-containing, neutron absorbing, thin films with simultaneous favorable mechanical, thermal, and electrical properties.

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