A new polymorphic material? Structural degeneracy of ZrMn$_2$

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Based on density functional calculations, we propose that ZrMn$_2$ is a polymorphic material. We predict that at low temperatures the cubic C15, and the hexagonal C14 and C36 structures of the Laves phase compound ZrMn$_2$ are nearly equally stable within 0.3 kJmol$^{-1}$ or 30 K. This degeneracy occurs when the Mn atoms magnetize spontaneously in a ferromagnetic arrangement forming the states of lowest energy. From the temperature dependent free energies at T $\approx$ 160K we predict a transition from the most stable C15 to the C14 structure, which is the experimentally observed structure at elevated temperatures.

Polymorphism of a solid material is its property to exist in several or even many crystal modifications which are called polytypes. A very famous example of a polymorphic material is SiC [1] for which the polytypes are distinguished by the variations of stacking of SiC bylayers. ZnS, as well, appears in many polytypes [2]. First principles calculations (as usual referring to T=0K) on SiC [3] and on ZnS and related II-VI compounds [4] revealed that the occurrence of polytypism must be due to the energetical degeneracy of structures at very low temperatures. For Laves phase compounds [5] so far only stability in the analysis of elastic and vibrational properties which strengthens our argument that ZrMn$_2$ is a truly polymorphic material.

For the calculation of ground state properties of ZrMn$_2$ in the C14, C15 and C36 crystal structures we applied density functional theory (DFT) by means of the plane wave Vienna Ab initio Simulation Package (VASP) [11] which -in its projector augmented wave formulation - is one of the most precise methods for calculating the energetics and electronic structure of solid matter within periodic boundary conditions. For the many-body exchange-correlation interaction the generalized gradient approximation of Perdew and Wang [12] in combination with the approach of Ref. [13] for spin polarization was chosen. The calculations are free from any empirical parameters. Lattice parameters as well as the atomic coordinates are determined by minimizing total energies and atomic forces. Care was taken that for each structure a sufficient number of k points for the Brillouin zone integration was chosen. Ferromagnetic as well as some selected antiferromagnetic spin arrangements were considered. Details will be described elsewhere [14]. In order to take into account the temperature dependent effects of lattice vibrations, the phonon dispersion and density of states were calculated by the so-called direct approach [15] utilizing data of VASP calculations. Furthermore, elastic constants for the C14 and C15 structure were determined from DFT energy densities corresponding to suitable distortions. The energy of formation was obtained from the difference of total energies for the compound and the pure phases [16].

Figure 2 contains the essential information of our study. Viewing the nonmagnetic (NM) results, clearly the energy...
of the C14 structure is lowest for all volumes. At equilibrium volume \( V_0 \) corresponding to the minimum of the energy curves C14 is favoured by about 1.5 kJ mol\(^{-1}\) compared to C36, and by the substantially larger amount of 5.3 kJ mol\(^{-1}\) compared to C15. The important role of magnetism is already illustrated by the results for the most stable cases of selected antiferromagnetic (AF) spin arrangements. For all structures, the minimum energies are lowered, lying now much closer together as compared to the NM case, with C36 as the favored structure. Also noticeable is that the equilibrium volumes for C14 and C15 are quite different expressing different magneto-volume effects. The most striking result is presented by the ferromagnetic (FM) data. Again, the energy is lowered for all structures when compared to AF, but now C14, C15, and C36 nearly coincide. By the very small energy difference of 0.3 kJ mol\(^{-1}\) (corresponding to \( \approx 30\text{K} \)) the cubic C15 phase is now more stable than the two hexagonal cases. At larger volumes, differences are getting slightly larger, whereas at smaller volumes (i.e. under pressure) the energy curves of all three structures are becoming undistinguishable.

The interpretation of these results is that for the crystallization process at least at very low temperatures there is a choice between at least three structures distinguishable by the stacking sequences according to Fig. 1. If one wants to fabricate low temperature polytypes of ZrMn\(_2\), molecular beam epitaxy seems to be the only choice. Standard procedures of bulk crystal growth are rather unsuitable for the creation of low temperature polytypes, because at high temperatures ZrMn\(_2\) crystallizes only in the C14 structure as observed at about 870K. On cooling down the C14 structure might be frozen in as a metastable state. The thermodynamical equilibrium, which according to our prediction is the C15 structure, might be never reached in a finite time. In addition, no simple deformation path can be imagined to deform C14 to C15 or C36, making a structural transition even less probable. At present, no unambiguous experimental structural information for low temperatures is available.

For ZrMn\(_2\), Stoner’s theory predicts the occurrence of band magnetism already from the NM density of electronic states at Fermi energy. The energetical degeneracy of structures then occurs for the ferromagnetic (FM) case. The most important indication why this happens is revealed by the right panel of Fig. 2. The FM energies for the corresponding \( V_0 \) are almost lying on one line quite in contrast to the NM case for which the C15 energy is rather high compared to C14. By spontaneous FM spin polarization all three structures gain different magnetization energies defined by \( U_{DFT}(FM; V_0) \)
\( U_{DFT}(NM; V_0) \), which are just of the right size to make the structures degenerate. The largest magnetization energy of 9.2 kJ mol\(^{-1}\) is gained in the cubic C15 structure. The degeneracy clearly is due to an electronic effect, since the structural changes, when relaxing geometries for all the magnetic states, have only insignificant influence on the energy differences. The average magnetic moment of Mn in all cases is about 0.9 \( \mu_B \). It should be noted, that for the hexagonal cases, not all Mn atoms are equivalent, therefore also the magnetic moments differ significantly. The average magnetic moments, however, agree very well between the structures. For the C14 structure the magnetic moments of the two non equivalent Mn atoms are 1.24 and 0.60 \( \mu_B \), for C15 the Mn moment is 0.90 \( \mu_B \), and for the C36 case three non equivalent Mn atoms appear with moments of 1.14, 0.92 and 0.71 \( \mu_B \). In contrast to other compounds with long range atomic stacking sequences [17], which are non magnetic, for ZrMn\(_2\) the ferromagnetic spin ordering for the energetical degeneracy of suitable atomic stackings is crucial.

Concerning antiferromagnetic spin orderings, it might be possible that more complicated AF structures (including non collinear spin arrangements) might lower the AF total energy. However, also due to the rather small magnetic moment we would not expect any substantial change of our findings that FM is the most stable phase. In any case, the structural degeneracy for FM ZrMn\(_2\) would be unaffected.

So far, the polymorphism of ZrMn\(_2\) is a predicted property based on calculated data. The question is how reliable are the results derived by the applied ab initio approach? An established fact is the occurrence of the C14 structure at elevated temperatures, which can be explained by our theoretical approach on taking into account the lattice vibrations. From the calculated phonon dispersion relations and phonon densities of states for C14 and C15 the temperature dependent free vibrational energy \( F_{vib}(T) \) is derived. Based on the difference curves in Fig. 3 we predict a structural phase transition C15 \( \rightarrow \) C14 at a transition temperature of \( T_{tr} \approx 160K \). A temperature dependent free energy contribution for the electrons was included as well [18], which, however, is unimportant at \( T = T_{tr} \). For temperatures larger than \( T_{tr} \), C14 is stabilized at least in comparison to the C15 structure. (Because of its large unit cell we did not calculate the phonon dispersion relations for C36) Decomposing the free energy \( F_{vib} = U_{vib} \) - \( TS_{vib} \) in contributions due to the internal energy \( U_{vib} \), and the entropy \( S_{vib} \) we find that the C15 \( \rightarrow \) C14 transition is caused by the vibrational entropy. Already the zero point energy \( F_{vib}(T = 0) \) contribution reduces the energy difference between C14 and C15. Although the C14 and C15 structures are nearly energetically degenerate no indication of any structural instability is seen in the phonon dispersion relations [14] as would be typical for martensitic transformations [8]. Finally, the elastic constants calculated for the C14 and C15 structures are typical for stable Laves phase compounds [14] and from the conditions for mechanical stability against any homogeneous elastic deformations [19] such instabilities can be excluded for both structures.

![FIG. 3: Difference of free energies \( F(C14) - F(C15) \) of ZrMn\(_2\) in the ferromagnetic state. Shown are results with contributions of lattice vibrations only (full line) and also with including electronic contributions (dashed line). Positive values: C15 structure is preferred; negative values: C14 is stable. Insert magnifies region around the temperature \( T_{tr} \) of the structural transition C15 \( \rightarrow \) C14.](image-url)
phase instability can be inferred. The available experimental information of -48 kJmol\(^{-1}\) in Ref. \[23\] needs to be checked by more recent experiments. The strong formation energy of ZrMn\(_2\) is quite in contrast to the very closely related compound YMn\(_2\). From standard DFT calculations we derive even slightly positive formation energies, and experimentally the compound hardly forms \[14, 22\]. The reliability of our calculated energies of formation is confirmed by the results for TiMn\(_2\) of about -90 kJmol\(^{-1}\), on which experiment and theory agree very well \[16\].

For the C14 structure of ZrMn\(_2\), for which experimental data exists, the calculated structural and lattice parameters are in good agreement with experiment \[14\]. The calculated volume is slightly smaller by about 3.4% possibly due to the approximations made for the many-body term of DFT. It should, however, be noted that the deviations are small and that our basic findings of energy degeneracy involve differences of energy, each of them obtained with the same approximations. Furthermore, the quality of our data is corroborated by the calculated energies of formation which in many cases agree with reliable experimental data. Very recently, ab initio DFT calculations for the C14 and C15 structures of ZrMn\(_2\) were published \[24\]. We find perfect agreement for the magnetic moment but -due to the lack of published data- no comparison of structural energy differences is possible.

Summarizing our results, based on density functional calculations we predict ZrMn\(_2\) to be polymorphic at low temperatures. We propose the degeneracy of at least three crystal structures (C14, C15, C36) which are distinguishable by different stacking of layers. This degeneracy occurs in the ferromagnetic phases, which are lowest in energy compared to nonmagnetic or selected antiferromagnetic spin orderings. The gain in magnetization energy due to spontaneous spin polarization is different for all investigated structures but just of the right size to cause the degeneracy. The C15 structure is stable by a very small energy difference which might disappear when pressure is applied. Including the free energies of lattice vibrations we predict a structural phase transition at 160 K to the C14 structure which is found experimentally at elevated temperatures. The structural degeneracy is not due to any instability: the phonon dispersions for the C14 and C15 structures show no soft modes, the energy of formation indicates strong bonding, and the elastic constants for C14 and C15 exclude any weakness due to elastic deformations. Finally, the reliability of our calculations is confirmed by comparison to reliable experimental data, for related compounds as well.

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