AN(N)^{N}I model for stacking fault energies in magnesium

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We apply the AN(N)^{N}I model to polytypes of magnesium with ideal axial ratio, and calculate the energies of four types of stable stacking faults in the basal plane. We find that the interaction energies between neighbouring layers decay as further neighbours are taken into account, although not converging to zero. A main dependence of the stacking fault energy on first-neighbour interaction is evidenced, and a hierarchy of the energies is established. The discrepancies between results obtained from different combinations of structures are discussed, and uncertainties on the values are estimated. The model is then extended to a number of magnesium alloys, and results are compared with the literature, with controversial outcomes.

Industrial interest in magnesium has been growing for the past few years and continues to do so, mainly due to its light weight (it is 30% less dense than aluminium and 75% less dense than steel); moreover, its alloys present remarkable properties such as high strength, good corrosion resistance and high versatility [1]. The widespread use of magnesium and its alloys in industrial applications (e.g. in the automotive industry and medical advances [2]) implies that research in this field focuses on the understanding of the mechanical properties of this metal and how they can be improved by adding alloying elements to magnesium. This includes the study of stacking fault energies and their dependence on factors such as temperature. Stacking faults are crystal defects characterised by the misplacement of crystallographic planes with respect to the periodic stacking sequence of the crystal; knowledge of their energies constitutes a useful tool in understanding the plastic deformation mechanisms of metals [3]. For hcp magnesium, whose correct stacking sequence is $ABAB...$ [4], there are four stable stacking faults in the basal plane. The first intrinsic stacking fault I_1 (or growth fault), is obtained through the removal of a basal plane, followed by the shear of the crystal above the fault of $\frac{1}{3}$ in the $[\bar{1}100]$ direction [5]. The second intrinsic stacking fault I_2 (or deformation fault) is formed by a shear in the $[\bar{1}100]$ direction [5]. The extrinsic stacking fault E is obtained by inserting an extra plane in the perfect sequence [5]; the twin-like fault T_2 possesses mirror symmetry about the fault plane [6] and is formed by replacing an A plane with a C plane [3]. Experimental measurements of SFEs are notoriously complicated to carry out due partly to their small magnitudes, and results obtained in the past have only managed to establish upper bounds on the energies. For this reason, in the literature research on Mg SFEs has relied heavily on first-principle calculations based on density functional theory (DFT) [7], with the main approach being that of the supercell method [6]. While the use of supercells has produced accurate results, it is often computationally demanding as well as involving complicated geometries. Moreover, SFEs calculated using supercells depend on factors such as the supercell size, the choice of k-mesh and the basis set.

An alternative method that avoids the drawbacks of the supercell method involves the use Ising-like models. The structural energy of a crystal can be defined as the sum of the interaction energies between layers plus a contribution coming from the energy of the system when interactions are not considered. A spin $S = \pm 1$ is assigned to the ith layer, according to whether the layer $i+1$ follows the "correct" stacking sequence or not. Conventionally, we assert that the correct stacking sequence is ABC, whereas the incorrect one is CBA. Consequently, the energy of a crystal with an arbitrary stacking sequence is expressed as follows:

$$E = E_0 - \sum_n^{N-1} J_n \sum_i^N S_i S_{i+n} \tag{1}$$

with E_0 being the energy of the system when all interactions between layers are ignored and N being the number of layers, where the assumption is that the magnitude of the interaction energy between neighbours decreases as n increases. In the ANNNI (Axial Next Nearest Neighbour Ising) model [8] interactions up to J_2 are taken into account; we propose to observe the behaviour of the J parameters as further neighbours are taken into account, using the AN(N)^{N}I model(s), with $N = 1, 2, 3, 4$ depending on how many neighbours are included. The sums in equation 1 can be evaluated for perfect structures straightforwardly; we have chosen five structures, classified in terms of the type of unit cell as in the case of the polytypes of silicon caribide [9]:

$$E_{3C} = J_0 - J_1 - J_2 - J_3 - J_4 \tag{2}$$

$$E_{2H} = J_0 + J_1 - J_2 + J_3 - J_4 \tag{3}$$

$$E_{4H} = J_0 + J_2 - J_4 \tag{4}$$

$$E_{6H} = J_0 - \frac{1}{3}J_1 + \frac{1}{3}J_2 + J_3 + \frac{1}{3}J_4 \tag{5}$$

$$E_{9R} = J_0 + \frac{1}{3}J_1 + \frac{1}{3}J_2 - J_3 + \frac{1}{3}J_4 \tag{6}$$

Where J_0 is the energy of one layer if interactions are not taken into account. The same can be done for crystals

containing stacking faults by describing them as limiting structures with periodic behaviour, as in [10], e.g. obtaining for I_1

$$E_{I_1}(N) = J_0 + \frac{N-2}{N}J_1 - \frac{N-4}{N}J_2 + \frac{N-6}{N}J_3 - \frac{N-8}{N}J_4 \quad (7)$$

The stacking fault energies are then defined in [11] as the excess energy compared to the perfect crystal:

$$\Delta E_{SFE} = \lim_{N\to\infty} 2N[E_{SFE}(2N) - E_{hcp}] \quad (8)$$

Where $2N$ is the periodicity of the crystal.
Applying this to equation 7 and similarly for the other faults, we obtain

$$\Delta E_{I_1} = -2J_1 + 4J_2 - 6J_3 + 8J_4 \quad (9)$$
$$\Delta E_{I_2} = -4J_1 + 4J_2 - 4J_3 + 4J_4 \quad (10)$$
$$\Delta E_{E} = -6J_1 + 4J_2 - 6J_3 + 8J_4 \quad (11)$$
$$\Delta E_{T_2} = -4J_1 + 8J_2 - 8J_3 + 8J_4 \quad (12)$$

as found by [12]. The J-parameters can be expressed in terms of the energies of the perfect structures, and the SFEs can be calculated indirectly, without having to compute the energies of the structures containing the stacking faults, and thus eliminating the drawbacks of the supercell model. The SFE is then given as energy per unit area [11], such that $\gamma = \frac{\Delta E}{A}$ with A being the area that defines the unit cell in one layer, $A = \frac{\sqrt{3}}{2}a^2$, a being the lattice constant.
To calculate the energies of the polytypes of Mg we use DFT as implemented in the Questaal (Quasiparticle Electronic Structure and Augmented LMTOs) suite of electronic structure simulation programs [13] exploiting the full potential Linear Muffin Tin Orbital (FP-LMTO) method [14] based on smooth Hankel functions [15]. For the calculation of exchange and correlation potential we use the generalised gradient approximation (GGA) [16] with the PBE (Perdew-Burke-Ernzerhof) functional. For the integration of the Brillouin zone we use a $30 \times 30 \times 30$ k-mesh and tetrahedron integration method [17] [18], and perform the self-consistent cycle using the Hohenberg-Kohn functional. To calculate the energies of the polytypes of Mg, we use a two-atom cell (2H), a one-atom cell (3C), a four-atom cell (4H), a six-atom cell (6H) and a nine-atom cell (9R), all with ideal axial ratio (1.633) and constant cell volume per atom (155.3163 au^3). Combinations including a number of polytypes can be constructed for each number of neighbours in each model as per table I.

N	combination (t) \ structure	2H	3C	4H	6H	9R
1	A	X	X			
	B	X		X		
	C	X			X	
	D	X				X
	E		X	X		
	F		X		X	
	G		X			X
	H			X	X	
	I			X		X
	J				X	X
2	K	X	X	X		
	L	X		X	X	
	M	X		X		X
	N	X			X	X
	O		X	X	X	
	P		X		X	X
	Q			X	X	X
	R	X	X			X
	S	X	X		X	
	T		X	X		X
3	U	X	X	X	X	
	V	X		X	X	X
	W	X	X	X		X
	X		X	X	X	X
	Y	X	X		X	X
4	Z	X	X	X	X	X

TABLE I. In this table the possible combinations of polytypes are defined. Here n refers to the number of neighbours included. A letter of the latin alphabet is assigned to each combination of polytypes.

For each combination the energies are then used to calculate the J-parameters for Mg, and the stacking fault energies are inferred. Results for the J-parameters and the SFEs are reported in tables II and III. We then use the supercell model as described in [19] to calculate the energy of the fault I_2 with ideal axial ratio, using a $1 \times 1 \times 12$ 24-atom supercell, a $30 \times 30 \times 20$ k-mesh, the Methfessel-Paxton sampling integration [20] and performing relaxation along the z-axis. Moreover, we study the behaviour of diluted Mg-Li, Mg-Ca and Mg-Zn alloys, using 64-atom (1.56% concentration of Li, Ca, Zn) and 128-atom (0.78% concentration of Ca) and including up to nearest neighbour interaction, thus calculating the energies of the 3C and 2H polytypes only. We employ a $20 \times 20 \times 20$ k-mesh, Methfessel-Paxton sampling integration and perform relaxation in all directions; we carry out a non-self consistent calculation using the Harris-Foulkes functional [21] [22].

N	1							
J_n \ t	A	B	C	D	E	F	G	H
J_1	−6.6	−5.9	−6.5	−4.3	−7.3	−6.7	−7.7	−8.3

N	2						3	
t / J_n	I	J	K	L	N	P	Q	R
J_1	−9.0	−8.6	−6.6	−7.1	−8.6	−8.6	−8.6	−6.6
J_2	-	-	−0.3	−0.6	−2.1	0.9	0.2	−1.1
J_3	-	-	-	-	-	-	0.3	0.8

N	3							4
t / J_n	S	T	U	V	W	X	Y	Z
J_1	−6.6	−8.1	−6.8	−6.3	−7.3	−7.9	−7.1	−7.1
J_2	−0.1	0.4	−0.3	0.2	−0.3	0.2	−0.6	−0.3
J_3	-	-	0.3	0.8	0.8	0.3	0.5	0.5
J_4	-	-	-	-	-	-	-	−0.2

TABLE II. This table shows the results obtained for the J parameters for each combination of structures, given in meV/atom.

N	1										2	
t / γ	A	B	C	D	E	F	G	H	I	J	K	L
γ_{I_1}	23.9	21.4	23.6	15.8	26.4	24.5	27.9	30.2	32.6	31.4	21.4	21.4
γ_{I_2}	47.8	42.8	47.2	31.6	52.8	49.0	55.9	60.3	65.2	62.8	45.3	47.1
γ_E	71.7	64.2	70.8	47.4	79.2	73.5	83.8	90.5	97.8	94.1	69.2	72.8
γ_{T_2}	47.8	42.8	47.2	31.6	52.8	49.0	55.9	60.3	65.2	62.8	42.8	42.7

N	2						3					4
t / γ	N	P	Q	R	S	T	U	V	W	X	Y	Z
γ_{I_1}	15.8	38.2	32.5	15.8	23.2	32.5	19.5	15.8	15.8	26.9	15.8	13.9
γ_{I_2}	47.1	69.5	63.9	39.6	47.1	45.3	62.0	41.6	45.3	56.4	43.4	43.4
γ_E	78.4	100.9	95.2	63.5	70.9	91.4	69.2	61.8	69.2	84.0	67.3	65.5
γ_{T_2}	31.5	76.4	65.1	31.5	46.5	65.1	40.9	37.2	37.2	55.7	35.3	35.3

TABLE III. This table presents the results obtained for the energies of the four types of stacking faults calculated via the AN(N)$^{\mathrm{N}}$I model using various combinations of polytypes. The SFEs are calculated in terms of energy per unit area (γ) and given in units of mJ/m^2.

From table II the averages of the J-parameters are found to be $\bar{J}_1 = -7.3 \pm 0.5$ meV, $\bar{J}_2 = -0.3 \pm 0.4$ meV, $\bar{J}_3 = 0.5 \pm 0.1$ meV, where the error represents the fluctuation in the data. It can be noted that the uncertainty is largest on J_2, whose value oscillates greatly between positive and negative values. while the hierarchy of the J-parameters does not always follow the predicted one, J_1 is nearly always at least one order of magnitude greater than the other coefficients. In the literature, Hu and Yang in [10] found $J_1 = -8.6$, $J_2 = -1.3$ and $J_3 = -0.7$ meV, for calculations performed using the local spin density approximation (LSDA) and $J_1 = -8.2$, $J_2 = -1.3$, $J_3 = -0.7$ meV using the GGA with PBE functional. However, they used axial ratios 1.599 (LSDA) and 1.600 (GGA), which are not only far from ideal, but also from the experimentally calculated ratio, i.e. 1.623 [10].
From the results displayed in table III, the hierarchy of SFEs can be observed. The energy of the E fault is the highest one, whereas the lowest is that of I_1. This could already be predicted by looking at equations 9 to 12, and is in agreement with the literature [10] [23] [24] [6] [3] [25]. However, in the literature, in which the supercell method is used, T_2 is found to have higher energy than I_2; in our data, to first order in J they are the same, whereas to higher order γ_{T_2} is often lower than γ_{I_2}. This finds confirmation in the paper by Hu at al. [10] quoted above, who use the ANNNI model. For this reason, this might be interpreted as a feature of an Ising-like description. Since the magnitude of the energy of the stacking fault determines its stability [10], it can be predicted that the occurrence of I_1 is more likely than that of E; generally, the two stacking faults more likely to occur should be I_1 and I_2, which are also the most stable. In addition, as is pointed out by Chetty and Weinert in [6], a T_2 fault is likely to decay into two I_1 faults, which have lower energies, and an E fault should decay into I_1 and I_2 faults. Through error propagation, the error on the SFEs is found as $\Delta\gamma_{I_1} = 3.6$ mJ/m^2, $\Delta\gamma_{I_2} = 4.7$ mJ/m^2, $\Delta\gamma_E = 6.3$ mJ/m^2 and $\Delta\gamma_{T_2} = 7.0$ mJ/m^2, where the uncertainty on γ_{T_2} is larger than that on γ_E due to its larger dependence on J_2. It can be noted that there is a convergence issue of the SFE; the energy of I_2 seems to converge as more neighbours are taken into account, but the energies of the other three faults tend to oscillate and then become smaller as n increases. This is due to J_2, J_3 and J_4 being all of the same order of magnitude; although the magnitude of the J coefficients decreases steeply after J_1, it does not decay to very small values fast enough for the SFE to converge. On the other hand, it can be seen that the SFE depends mainly on J_1; this is more evident for I_2.
Qualitative comparison can be drawn with the literature, where the supercell method was used, along with DFT-calculated axial ratios. Refs [24] and [6] used the plane wave pseudopotential method, respectively within the GGA with PBE functional and withing the LDA. The projector augmented wave (PAW) method [26] along with the GGA with the PW91 functional [27] were used by refs [23] and [28], whereas refs [25] and [29] used the PBE functional. Ref [19] used the same FP-LMTO method that we used, along with the GGA with the PBE functional. The results obtained are in good agreement with each other, especially in the case of the I_2 fault. In our case, the SFEs for I_1 and T_2 were found to be lower than those calculated in the literature, whereas those of I_2 and E are nearly always higher. From our supercell calculation of the SFE for I_2 with ideal axial ratio we obtain $\gamma_{I_2} = 44.5$ mJ/m^2, which is in agreement with the energies calculated using 14 out of 24 combinations with the AN(N)^{N}I model.

Table IV reports the results for the SFEs of four binary alloys. In the literature, ref [30] reported that a low concentration of zinc should leave the SFE essentially unchanged, while the addition of lithium to magnesium should increase the SFE, for $\sim 2\%$ concentrations; ref [31]

γ \ alloy	Mg-1.56%Li	Mg-1.56%Ca	Mg-1.56%Zn	Mg-0.78%Ca
γ_{I_1}	24.2	27.7	22.2	26.8
γ_{I_2}	48.4	55.4	44.4	53.6
γ_E	72.5	83.1	66.7	80.3
γ_{T_2}	48.4	55.4	44.4	53.6

TABLE IV. This table presents the results obtained for the energies of the four types of stacking faults in Mg alloys calculated via the ANNI model (all concentrations are atomic). The SFEs are calculated as energies per unit area (γ) and given in units of mJ/m^2 [11].

presented similar conclusions, reporting however only a very small increase in the case of the addition of lithium, for low concentrations. In [32], the addition of zinc at $\sim$ 1% concentration reportedly resulted in a small increase of the SFE for I_1 and I_2. Overall, as observed by Andritsos et al. [19], low concentrations of Li and Zn in Mg should not affect the SFE greatly. If we take the SFEs calculated for combination A as the reference energies for pure Mg, we observe that in our case the addition of Li causes essentially no change in the SFE, while the addition of Zn slightly decreases it. Concerning Mg-Ca diluted alloys, the literature predicts a decrease in the stacking fault energy with respect to pure Mg; this is the case for [31], [33] ($\sim$ 1% concentration) and [34] (0.78% and 0.69% concentrations). From our data we report instead a significant increase in the SFE for both concentrations.

In conclusion, we have investigated the validity of the AN(N)^{N}I model(s) for the calculation of stacking fault energies in Mg with ideal axial ratio, as well as in a number of Mg alloys. Although a main dependence of the SFE on nearest neighbour interactions was reported, further neighbour interactions were not found to decay quickly enough for the SFE to converge. In the case of alloys, the way in which the SFE is affected by the addition of diluted alloying elements was studied, with results in partial agreement with the literature. Overall, the AN(N)^{N}I model emerged as viable alternative to the supercell method, and as a worthy object of further investigation and study.

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