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Structural, thermal, and magnetic properties of Ni₂MnGa

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The two main effects underlying the magnetic shape memory effect in Ni₂MnGa are martensitic transformations and magnetic anisotropy energies. Both issues are addressed here with first-principles calculations. First, we examine how the tetragonality in the martensitic phase varies with the composition. Then, the actual transformation is investigated by comparing the free energies of different phases. The transition from the cubic structure to the tetragonal structure with $c/a = 1.27$ is driven by the vibrational free energy and occurs at a temperature of 200 K which is in the experimental range. Finally, we focus on the magnetic anisotropy energy for the tetragonal structure with $c/a = 0.94$. It is shown to be a magnetically nearly ideal uniaxial system determined by the first-order anisotropy constant. However, it is estimated that the twinned microstructure can cause higher-order anisotropies to show up in the measured anisotropy. © 2002 American Institute of Physics. [DOI: 10.1063/1.1453933]

Magnetic shape memory (MSM)¹ alloys are attaining interest as possible smart materials which can function both as actuators and as sensors. The MSM effect is due to a magnetic field induced redistribution of twin variants in a martensitic phase.² The MSM effect offers faster response compared to conventional temperature driven shape memory alloys. In addition, the obtained strains are much larger than in ordinary magnetostrictive materials. Ni–Mn–Ga alloys close to the stoichiometric composition Ni₂MnGa have shown large deformations up to 6% under magnetic field.³ The two main ingredients in this phenomenon are the martensitic transformation and the magnetic anisotropy energy in the martensitic phase which are studied here with first-principles calculations.

In the high temperature phase Ni–Mn–Ga alloys have the cubic L2₁ structure as shown by x ray and neutron diffraction measurements.^{4,5} In the low temperature range, different martensitic phases appear depending on the composition and temperature.⁶ The symmetry of martensitic structures is lower than the cubic one, and these phases can have a twinned microstructure. At the moment the MSM effect is realized in the phase with a tetragonal structure where the ratio of lattice constants $c/a \sim 0.94$. There is also interest to study another phase where $c/a \sim 1.2$ because the maximum available strain is determined by the c/a ratio. The actual c/a ratios vary with the composition, as well as the transformation temperatures which range from 200 K to over 600 K.⁶ We study here this variation of c/a and relate it

with the electronic structure. Also, we investigate the martensitic transformations in the stoichiometric composition and aim to determine the ideal transformation temperatures.

Both the cubic and tetragonal phases are ferromagnetic with the magnetic moment confined mainly in the Mn sites as shown by neutron diffraction experiments⁵ and theoretical calculations.⁷ While the magnetization curve measurements^{8–10} have suggested that the anisotropy of these tetragonal structures is uniaxial, the angular dependence of the anisotropy has not yet been studied. Here we examine this angular dependence in the case $c/a = 0.94$.

The calculations are based on the density-functional theory employing the full-potential linearized augmented plane wave (FLAPW) method¹¹ as implemented in WIEN97.¹² The computational details are explained in Ref. 13. The volume of the unit cell is fixed to the theoretical volume of the cubic structure⁷ in the following.

As a first step we investigate the structural properties of the ground state at zero temperature. For the stoichiometric Ni₂MnGa alloy, three energy minima can be found with different tetragonal distortions which correspond to the cubic, $c/a = 0.94$, and $c/a = 1.27$ structures. However, as most experiments are done with nonstoichiometric samples, the effects of composition have been modeled within the rigid band approximation. It is found that the energy differences between the structures vary with band filling. Also the c/a value corresponding to the energy minimum depends on stoichiometry. Although the variation is small for $c/a < 1$, the differences are clearly visible for $c/a > 1$ as seen in Fig. 1. In the latter case the optimum c/a ratio increases first with the

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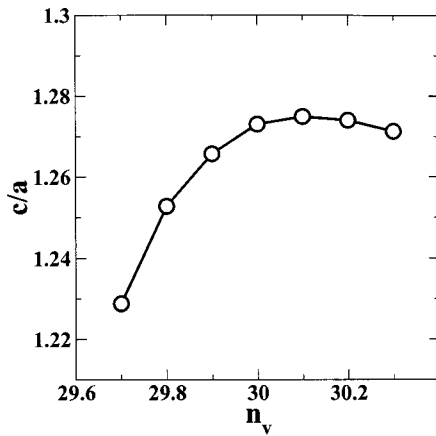


FIG. 1. Optimal tetragonality ratio c/a as a function of band filling n_v for the $c/a > 1$ martensite.

band filling and, after reaching a maximum, it starts to decrease. This behavior can be understood by taking into account the electronic structure. The tetragonal minima are stabilized when electronic bands around the Fermi level split⁷ in a similar way to a Jahn–Teller like distortion. As the band filling changes the position of the Fermi level, the optimized c/a ratio changes also.

Next, the martensitic transformation is studied by calculating the free energy as a function of the temperature for the cubic structure and for the tetragonal structures $c/a=0.94$ and $c/a=1.27$. The free energy is divided into an electronic and a vibrational part. The electronic free energy can be obtained from a standard total energy calculation as

$$F_{\text{elec}}(T) = E(T) - TS, \quad (1)$$

where $E(T)$ is the total energy where the electronic states are weighted with the Fermi–Dirac distribution at temperature T . S is the electronic entropy given by¹⁴

$$S = -k_B \sum_i [f_i \ln(f_i) + (1 - f_i) \ln(1 - f_i)], \quad (2)$$

where f_i are the occupation numbers of the electronic states and the summation runs over occupied states and the Brillouin zone. The vibrational free energy is determined from the Debye model, whose parameters are obtained from first-principles calculations and experiments. Within this model, the vibrational free energy is given by¹⁵

$$F_{\text{vib}} = -k_B T \left(D(\theta_D/T) + 3 \ln(1 - e^{-\theta_D/T}) - \frac{9\theta_D}{8T} \right), \quad (3)$$

where $D(x)$ is the Debye function and θ_D is the Debye temperature. The Debye temperature is calculated according to Ref. 16 using the cubic elastic constants C' and C_{44} , and the bulk modulus B . Only the tetragonal shear deformation is considered here. As B and C_{44} are large compared to C' ,^{17,18} B and C_{44} are assumed to be the same in all three phases and only C' has different values. The elastic constants are obtained from earlier calculations.^{7,19} Summing up, the resulting free energies as a function of temperature are shown in Fig. 2. It is seen that the transition from the $c/a=1.27$ structure to the cubic one appears below 200 K which is in the

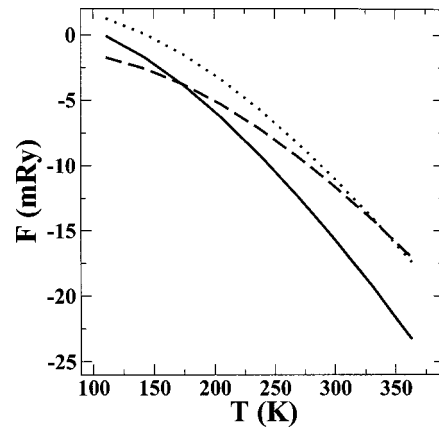


FIG. 2. Free energy as a function of the temperature. Solid line: cubic; dashed line: $c/a=1.27$; dotted line: $c/a=0.94$.

same range as the experimental transition temperatures. Here, the temperature dependence of the free energy comes mainly from the vibrational part so that the Debye model works surprisingly well. On the other hand, the free energy of the $c/a=0.94$ structure is not the lowest one at any temperature, so that the transition to this phase does not happen. It can be noted that a certain set of parameters in the above Debye model can produce the transition to the $c/a=0.94$ structure, so that the problem can be in the theoretical determination of these parameters. Also, besides the approximations made above, there are several other options which may affect these results. For example, magnetic or further structural degrees of freedom may play a role here.

Finally, we study the magnetic anisotropy for the $c/a=0.94$ structure. In a magnetically uniaxial material, symmetry arguments force this energy to have the form

$$E = K_1 \sin^2(\theta) + K_2 \sin^4(\theta) + \dots, \quad (4)$$

where K_1 and K_2 are the anisotropy constants and θ is the angle between the magnetization and the z axis. In most cases the K_1 constant is the dominant one. A system where the K_2 term and higher order terms are zero can be considered as an ideal uniaxial system. In order to clarify the uniaxiality of the martensitic phase, we have calculated the total energy as a function of the magnetization direction. The

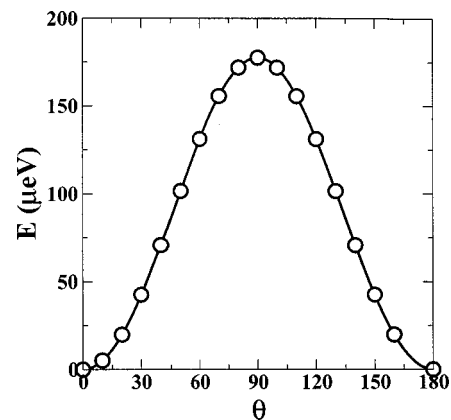


FIG. 3. Total energy as a function of the magnetization direction. Solid line is a fit to Eq. (4).

magnetization is varied in the $(1\bar{1}0)$ plane, and the resulting total energy is shown in Fig. 3. This curve shows a $\sin^2(\theta)$ behavior where the period of π is clearly seen. A fit of the calculated energies to Eq. (4) gives $K_1 = 170 \mu\text{eV}$ and $K_2 = -0.3 \mu\text{eV}$, so that the magnetic anisotropy is determined mainly by the constant K_1 .

On the other hand, the presence of the twinned microstructure in the martensitic phase can sometimes complicate the analysis of anisotropy measurements because several twins are often present. Therefore, we give an estimate for an equal amount of two twins by averaging over both twins. As the easy axes of the two twins differ by around 90° , the corresponding average energy is

$$E_{\text{ave}} = K_1 \sin^2(\theta) + K_2 \sin^4(\theta) + K_1 \sin^2(\theta + \pi/2) + K_2 \sin^4(\theta + \pi/2) = K_1 + K_2 [1 - 2 \sin^2(\theta) + 2 \sin^4(\theta)]. \quad (5)$$

It is seen that the angular dependence is completely due to the K_2 term. The uniaxial and fourfold anisotropies occur with the same strength but opposite signs and the periodicity is $\pi/2$ instead of π . As the order of magnitude of K_2 is equal to the magnetic anisotropy in the cubic structure, experiments can also show similar anisotropy constants in the twinned martensite and austenite. Although the real experiment would of course be more complicated than the above average, it is clear that measurements which involve several twins may produce a large contribution of the K_2 constant. Further experiments should be done in order to clarify this issue.

In conclusion, we have presented results based on first-principle calculations about the structural, thermal, and magnetic properties of Ni_2MnGa . The variation of the tetragonality c/a in the martensitic phase with the composition is shown to arise from the electronic structure via a Jahn–Teller-like effect. The transformation from the cubic to the $c/a = 1.27$ structure is found to be driven by the vibrational free energy. The theoretical transition temperature for the stoichiometric case is in good agreement with experiments. Finally, we clarified the uniaxiality of the magnetic anisotropy for the $c/a = 0.94$ structure, and showed how a twinned

microstructure can give rise to the contribution of higher order anisotropy constants.

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