

Quantitative Landau potentials for the martensitic transformation in Ni–Al

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The martensitic phase transformation in Ni–Al (63.5 at. % Ni) is described by a Landau-type Gibbs free energy $G(Q) = 1/2A\Theta_s(\coth(\Theta_s/T) - \coth(\Theta_s/T_C))Q^2 + 1/4BQ^4 + 1/6CQ^6$, with $A = 5.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $B = -3493 \text{ J mol}^{-1}$, $C = 4901 \text{ J mol}^{-1}$, $T_C = 86 \text{ K}$, and $\Theta_s = 257 \text{ K}$. The dispersion (Ginzburg) energy was estimated to be $g = 60 \text{ J mol}^{-1} \text{ nm}^2$. This potential was determined from high resolution diffraction data to determine the spontaneous strain as proxy for the order parameter Q and differential scanning calorimetry measurements for the calibration of the excess entropy of the martensitic phase transformation. The Gibbs free energy is compared with equivalent functions of Ni–Ti, quartz, KMnF_3 , BaTiO_3 , and SrTiO_3 . © 2007 American Institute of Physics.
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Most martensitic phase transitions in metals and alloys are strongly discontinuous, which limits the determination of order parameters besides its trivial values of zero in the austenite phase and a very narrow interval near unity in the martensitic phase.^{1,2} Intermediate values have no thermodynamic stability while they may still relate to unstable or metastable states. They may also be useful for any theoretical description of the transformation behavior based on analytical theories.^{3–9} Mathematical descriptions of potential functions of the martensitic state were often kept general for the relevant potentials (e.g., confined to narrow parabolic troughs near the equilibrium values) because no information can be obtained about the rest of the configuration space between the troughs.¹⁰

This situation is very different for ferroelastic materials, mainly oxides, silicates, phosphates, etc.^{11–19} which show phase transitions of a similar physical nature but with a large variation of the order parameters. The transitions are often continuous, which allows the experimental determination of the order parameter between zero and their maximum value at absolute zero temperature. In addition, their sometimes sluggish kinetic behavior allows the detailed analysis of non-equilibrium states. The continuous variation of order parameters has been well documented in many studies.¹¹ Their temperature evolution was found to be well described by Landau theory and their appropriate extensions,¹² while even the nonequilibrium states can be approximated by simple kinetic rate laws where driving forces are functional derivatives of the Landau potential. The bane in the research of continuous phase transitions is that thermodynamic fluctuations of improper ferroelastics, such as SrTiO_3 ,¹⁴ and in doped or strongly heterogeneous materials¹¹ can modify the behavior near the transition point.²⁰ Such fluctuations are suppressed in systems with elastic interactions with long correlation lengths leading to mean field solutions.²¹

It is the purpose of this letter to show that in martensites such as Ni–Al the temperature evolution of the strain and the specific heat is significant enough to test the hypothesis^{3–9}

that an analytical description of the excess Gibbs free energy of the phase transformation can be cast within the concept of Landau theory. We basically treat Ni–Al as a ferroelastic material such as SrTiO_3 , LaAlO_3 , or $\text{Pb}_3(\text{PO}_4)_2$ while accepting that a significant interval of the order parameter variation is not accessible experimentally because of the stepwise character of the phase transition. Evidence for the displacive nature of the transition in Ni–Al is based on early neutron diffraction studies of the dip in the acoustic dispersion near the critical point of the polytypic super structure^{22,23} and on the observation of acoustic anomalies compatible with the softening of the acoustic branch.²⁴ In this letter we argue that even the macroscopic order parameter follows an extended Landau-Ginzburg behavior^{12,25} in the displacive limit. For comparison we also analyzed the martensitic transformation in CuZnAl where the excess heat capacity below the transition temperature was below experimental resolution²⁶ so that no strain effects should occur if a Landau description is adequate.

Samples of NiAl with composition of 63.5 at. % Ni and 36.5 at. % Al and of CuZnAl with 65.16 at. % Cu, 23.52 at. % Zn, and 11.32 at. % Al had a characteristic size of $5 \times 5 \times 2 \text{ mm}^3$. The CuZnAl sample was a single crystal. The Ni–Al samples contained several grains with $\sim 1 \text{ mm}$ diameter and were annealed at 1473 K and quenched to room temperature. Samples with two different quench rates (samples I and II) showed different transition temperatures: Ni–Al (I) at 460 K and Ni–Al (II) at 240 K. Their transition temperatures were determined by differential scanning calorimetry (DSC) measurements (Perkin Elmer, model Diamond DSC) and by x-ray rocking curve measurements. The detailed experimental arrangements for the diffraction measurements are given in Ref. 27. The transition temperature in CuZnAl is 70 K.

The spontaneous strain of the Ni–Al samples was 13.5% at low temperatures which exceeds the value of the spontaneous strain in CuZnAl (10.3%). The data in Fig. 1 clearly show that the spontaneous strain in Ni–Al increases significantly when the sample is cooled through the transition temperature while the strain in CuZnAl remains essentially con-

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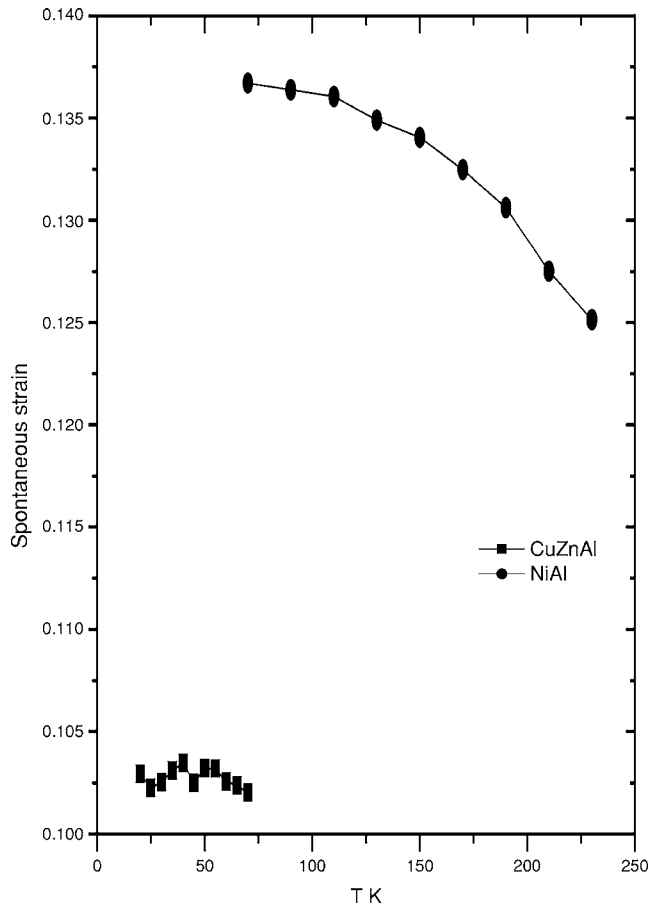


FIG. 1. Temperature evolution of the spontaneous strain in CuZnAl and Ni-Al (II).

stant. This is in good agreement with the observation that the excess entropy of the transition also increases with decreasing temperature in Ni-Al, while no such increase was found in CuZnAl in a previous study²⁶ (Fig. 2).

The driving order parameter Q in the β_2 phase of Ni-Al is coupled bilinearly²⁸ with the spontaneous strain e so that a diagonalization of the expression for $G(Q, e)$ via the strain-free condition $dG/de=0$ leads to an expression of $G(Q)$ which, omitting the vector notation of the order parameter and the spontaneous strain, corresponds to an effective thermodynamic potential of the form^{11,12}

$$G(Q) = 1/2A\Theta_s(\coth(\Theta_s/T) - \coth(\Theta_s/T_c))Q^2 + 1/4BQ^4 + 1/6CQ^6,$$

where Θ_s is the quantum mechanical saturation temperature, T_c is the Curie temperature, and A , B , and C are energy scaling parameters related to local potentials.¹² Here the expression is limited to sixth order potentials in order to keep the number of free parameters small; higher order terms were discussed in Ref. 4. The saturation temperature becomes relevant for data below room temperature.¹⁴ A first estimate for simple structures relates Θ_s to the thermodynamic Einstein temperature Θ_E via²⁸

$$\Theta_s = 1/2\Theta_E.$$

In the case of Ni-Al we take as starting value for the analysis an Einstein temperature of 500 K and set Θ_s at 250 K as initial value. A test for the validity of the approach follows from the scaling of the excess entropy which is related to the

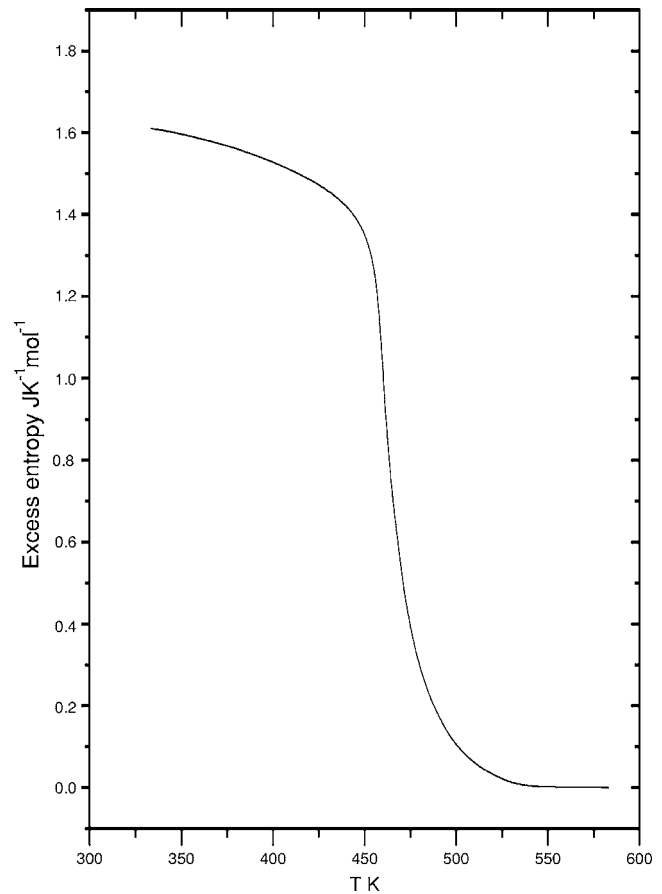


FIG. 2. Temperature dependence of the excess entropy of Ni-Al (I).

order parameter via $S(Q) = dG(Q)/dT$. At $T \gg \Theta_s$ this leads to $S = 1/2AQ^2$. As the spontaneous strain scales linearly with the order parameter we find, thus, the scaling $S \sim e^2$ which can be tested experimentally.¹⁴

The spontaneous strain can also be expressed explicitly in terms of the order parameter with the temperature dependence,

$$\left(\frac{e}{e_0}\right)^2 = \frac{-B + \sqrt{B^2 + 4AC\Theta_s(\coth(\Theta_s/T_c) - \coth(\Theta_s/T))}}{2C}.$$

In the $7R$ or $14M$ phase of Ni-Al the scaling relationships are more complex. The ground state is characterized by a sevenfold increase of the unit cell along the crystallographic $[001]$ direction.²⁹ This polytypic cell increase is assumed to contribute little additional energy to the excess Gibbs free energy as shown in the case of PbI_2 where such energy was measured directly.³⁰ We expect that the underlying stress energy is similar to the phase α' .²⁹ Under these plausible assumptions we can now analyze the temperature evolution of the spontaneous strain in the $7R$ phase in the same way as in the α' phase, namely, in bilinear coupling with the thermodynamic order parameter.

The experimental data were then fitted to the Landau parameters T_c , A , and B (the parameter C follows from the normalization condition at $T=0$ K). Θ_s was refined from its initial value within a narrow interval. The resulting parameters are summarized in Table I.

The thermodynamic potential of Ni-Al is consistent with all experimental equilibrium data as reported in this letter. The validity of the approach was checked for the case of

TABLE I. Landau parameters of some first order ferroelastic and coelastic phase transitions and the second order transition in SrTiO₃.

Compound	A (J K ⁻¹ mol ⁻¹)	B (J mol ⁻¹)	C (J mol ⁻¹)	T_c (K)	Θ_s (K)
Ni–Al (I)	5.6	–5038	7491	338	250
Ni–Al (II)	5.6	–3493	4901	86	257
Ni–Ti ^a	4.66	–320.4	375.5	282	
Ni–Ti ^b	10.9	–1758.8	4825.2	282	
KMnF ₃ ^c	2.78(1)	–57.4(6)	573(40)	185.76(1)	
Quartz ^{d,e}	9.8	–1921	10190	851	187
BaTiO ₃ ^f	4.53	–787.8	2568.8	391	160
SrTiO ₃ ^g	0.7	31.22	42.17	105.65	60.75

^aReference 31.^bCalculated from data of Ref. 31 with normalization condition $Q(0\text{ K})=1$.^cReference 32.^dReference 33.^eReference 34.^fReference 35.^gReference 14.

CuZnAl where no excess entropy was observed and, as expected, no variation of the spontaneous strain at low temperatures was found in this study. These observations give us confidence that the thermodynamic potential has physical reality and can be used to describe phase transformations in Ni–Al. The remaining term in the thermodynamic potential which can not be determined from our experiments is the Ginzburg energy $1/2g$ (grad Q)². This term can be estimated as follows. The width of a twin domain wall is given by the length scale $w=(2g/AT_C)^{1/2}$. With $AT_C=482\text{ J mol}^{-1}$ from Table I and the observation that the thickness of domain walls in martensites is only a few lattice parameters wide we set $w=0.5\text{ nm}$. The resulting dispersion parameter is $g=60\text{ J mol}^{-1}\text{ nm}^2$. This leads to the following full thermodynamic potential (in J mol^{-1}):

$$G(Q) = 720(\coth(257/T) - \coth(257/86))Q^2 - 873Q^4 + 817Q^6 + 30(\text{grad } Q)^2.$$

We can now compare this potential with others in Table I. In displacive transitions, the transition entropy and hence A is small compared with the configurational entropy $N\ln(N)$ where N is the relevant number of states. With $N=2$ as lowest value we typically find A in displacive systems to be in the order of $<10\text{ J K}^{-1}\text{ mol}^{-1}$. The relevant value of quartz is $9.8\text{ J K}^{-1}\text{ mol}^{-1}$. Strongly first order transitions display values of B in the order of -1921 J mol^{-1} for quartz and -57 J mol^{-1} for KMnF₃. The value of A for Ni–Al ($5.6\text{ J K}^{-1}\text{ mol}^{-1}$) is very much within the typical range of other displacive phase transitions including those with itinerant electronic states,³⁶ even the value of B is similar to those of quartz and BaTiO₃. These compounds have been thoroughly analyzed in terms of their respective Landau potentials. It is useful, therefore, to analyze the stepwise character of the phase transformation in Ni–Al within the same framework as the other compounds. The step in the order parameter at T_{trans} disappears when B approaches zero. This condition $B=0$ is called a tricritical point. The measure for the distance from the tricritical point is the parameter $B^2/4AC(K)$ which is then compared with the temperature T_C of the Landau potential. If we normalize this closeness parameter by T_C we find $B^2/4ACT_C=1.3$ in NiAl (II). This value is much greater than the same parameter for quartz (0.01), BaTiO₃ (0.03), and

Ni–Ti (0.05). This comparison shows that the transition in Ni–Al is much more strongly stepwise (and much further removed from the tricritical point) than those in the comparable ceramics and the $B2\rightarrow R$ -phase transition in Ni–Ti. Nevertheless, our results show clearly that the relevant thermodynamic Gibbs free energy is still well described within the framework of Landau potentials.

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