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Landau theory of structural transformations in titanium–nickel and gold–cadmium alloys

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Abstract

We present a rigorous symmetry-based Landau theory of the two martensitic transformations from the cubic B2 (β_2) austenite parent phase to the rhombohedral R (ζ_2') product phase of P3 symmetry and to the orthorhombic B19 (γ_2') product phase of Pmma symmetry. Both are improper ferroelastic transformations; their primary order parameters are expressed in terms of the shuffle displacements that correspond to the two [$\zeta\zeta$0] TA_2 modes for $\zeta = 1/3$ and $\zeta = 1/2$, respectively. Numerical agreement with experimental data is exact for the B2–B19 transformation and good/fair for the B2–R transformation in AuCd/TiNi, respectively.

Keywords: Martensitic transformations; Landau theory; NiTi; AuCd; B19 phase; R phase

1. Introduction

The prototype shape-memory alloys Ti–Ni and Au–Cd, and the pseudo-binary alloys Ti(Ni,X) (X = Fe, Al, Cu) undergo displacive phase transformation (PT) from the cubic B2 (β) austenite parent to a trigonal R (ζ_2'), an orthorhombic B19 (γ_2'), and (except Au–Cd) a monoclinic B19′ martensite phase [1]. Which of these PTs or transformation sequences occur depends on composition and thermo-mechanical treatment [2]. It has been recognized early that there is a correlation between the transformation strain and crystal structure on the one hand, and soft elastic moduli [3–5] and/or shuffle displacements corresponding to certain lattice waves on the other [5,6]. More recently, the relevance of these correlations has been substantiated by the observation of (partial) softening of the [$\zeta\zeta$0] TA_2 phonon modes for $\zeta \approx 1/3$ in TiNi [7], and for both $\zeta \approx 1/3$ and $\zeta = 1/2$ for Ti(Ni,Fe) [8,9] and Au–Cd [10,11]. Furthermore, through more accurate recent diffraction experiments, controversies on the space groups of the product phases have been resolved and a data basis for comparison with Landau theoretical models created [12–15]. In addition, the present paper was motivated by the fact that the Landau free energy (LFE) is a prerequisite for the description of twin boundaries and heterophase interfaces in terms of Landau–Ginzburg models that require inclusion of gradient terms of the primary order parameter (POP) [16,17].

2. Experimental background

The experimental [$\zeta\zeta$0] TA_2 phonon dispersion curves for two compositions of $Au_{1-x}Cd_x$ and for Ti–46.7 at%Ni–3.2 at%Fe exhibit mode softening with minima at $\zeta \approx 1/3$ and $\zeta = 1/2$; in Fig. 1a,b, the squares of the corresponding frequencies at these minima are plotted versus temperature and show softening that is mostly linear within the relatively large experimental error. For Ti(Ni,Fe), the wave vector at which the first minimum occurs is temperature dependent, and with decreasing temperature tends toward $\zeta = 1/3$ [8], signaling the disappearance of the incommensurate intermediate phase (cf. for example, the review in [18]). It is generally accepted that the PT to the R phase occurs when the wave vector locks into the commensurate value $\zeta = 1/3$.

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