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Structural Phase Transition in AuZn Alloys

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Abstract. Au_xZn_{1-x} alloys undergo a shape memory martensitic transformation whose temperature and nature (continuous or discontinuous) is strongly composition dependent. Neutron diffraction experiments were performed on single crystals of $x=50$ and 52 to explore the structural changes occurring at the transition temperature. A transverse modulation with wavevector $q_0=(1/3,1/3,0)$ develops below the transition temperature, with no observable change in lattice parameter. However, the Bragg peak width shows a broadening suggesting an unresolved rhombohedral distortion similar to what has been observed in NiTi-Fe alloys.

1. Introduction

Shape memory properties occur in materials undergoing martensitic phase transformation that are normally first order transitions showing an abrupt change in the lattice parameters at the transformation temperature. The transformation is diffusionless, reversible, with a very small volume change. The structure of the high temperature austenite phase of most shape memory materials is cubic and the low temperature martensite phase has a lower symmetry, either tetragonal, monoclinic or triclinic structure. The occurrence of many domains in the martensite phase is the key element of the shape memory properties.

Recently it was noted that the intermetallic alloy, Au_xZn_{1-x} undergoes a nearly continuous phase transformation for the 50-50 composition, but is first order at off-stoichiometric compositions [1]. Near the transition temperature, T_M , which is composition dependent, a transverse modulation of the lattice develops with wavevector $q_0=(1/3,1/3,0)$. Also, the transition temperature decreases with increasing pressure suggesting a quantum critical regime. [2].

Here we probe the structural transition in more detail in order to gain more insight into the low temperature structure and compare the behavior with the well studied Fe doped NiTi.

2. Experimental Details and Results

The single crystals of $\text{Au}_x\text{Zn}_{1-x}$ were prepared by fusion of elements in a Bridgman furnace. The $x=50$ sample was cut into a 1mm^3 cube with faces along the cubic direction and had a crystal mosaic of about 0.8° . The $x=52$ crystal was smaller with a slightly larger mosaic. The neutron experiments were performed on the BT9 triple-axis spectrometer at the NIST research reactor using an incident energy of 14.7 meV with filters placed in the beam. Because of the small size of the sample collimation of $40'$ was used throughout the instrument.

Figure 1 shows the temperature dependence of the satellite peak intensity measured at q_0 for $x=50$ and $x=52$. For $x=50$ the behavior is nearly continuous and can be fit with a power law with critical exponent $\beta=0.51$, consistent with mean field theory [2]. For $x=52$ the transition temperature is shifted to lower temperatures and is more discontinuous.

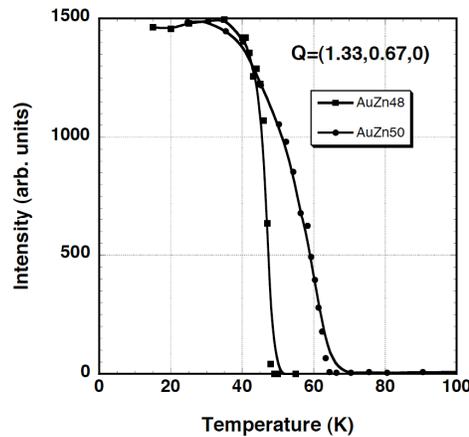


Figure 1. Temperature dependence of satellite intensity on heating for $\text{Au}_{1-x}\text{Zn}_x$: $x=50$ and $x=52$.

The transition temperatures measured are consistent with those obtained from specific heat and resistivity measurements [3]. Also, the nature of the transition: nearly continuous for $x=50$ and discontinuous for $x=52$ are also consistent with other measurements. In our experiment we monitored the $(1,1,0)$ Bragg peak in order to observe a change at the transition temperature. Figure 2 is a plot of the lattice parameter for $x=52$. Surprisingly, no anomaly is apparent near the transition temperature $T_M=48\text{K}$ where the satellite intensity begins to increase. A similar observation was made for $x=50$.

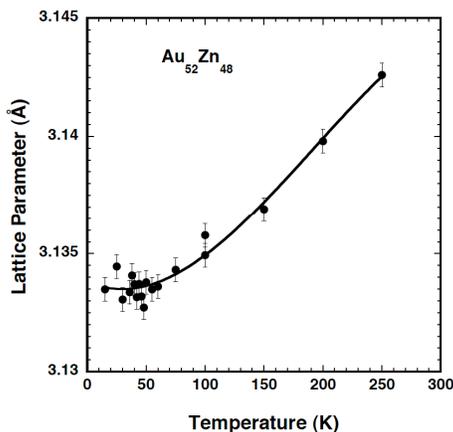


Figure 2. Lattice parameter for $\text{Au}_{53}\text{Zn}_{48}$ measured at the $(1,1,0)$ position vs temperature

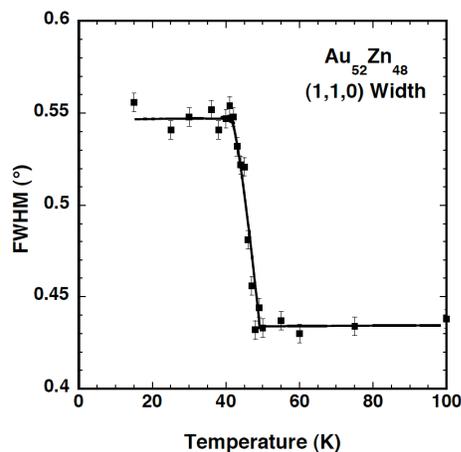


Figure 3. Angular width of longitudinal scan through $(1,1,0)$ Bragg peak.

However, the width of the Bragg peak did change abruptly at the transition as shown in Fig. 3, which is the angular width of a longitudinal $\theta-2\theta$ scan.

Another observation was the presence of the satellites measured in the [HKK] zone for $x=50$ at equivalent $q_1 = [1/3, 1/3, 1/3]$ satellite positions that appear below T_M . Mesh scans performed at 10K at several equivalent positions reveal an incommensurability that varied with satellite position. The temperature dependence of this incommensurability was not monitored to see if there was a lock-in.

3. Discussion

The high temperature phase of Au_xZn_{1-x} has the cubic CsCl structure. The low temperature phase was reported to be trigonal with $P3(C_3^1)$ space group [4]. The signature of this symmetry change is a splitting of the $(1,1,0)_C$ cubic Bragg peak into a $(1,1,2)_R$ and $(0,0,3)_R$ trigonal or R-phase Bragg peak. This is not happening in our samples (Fig. 2) and we conclude that the trigonal distortion is small and cannot be resolved, but shows up as broadening of the Bragg peak (Fig. 3)

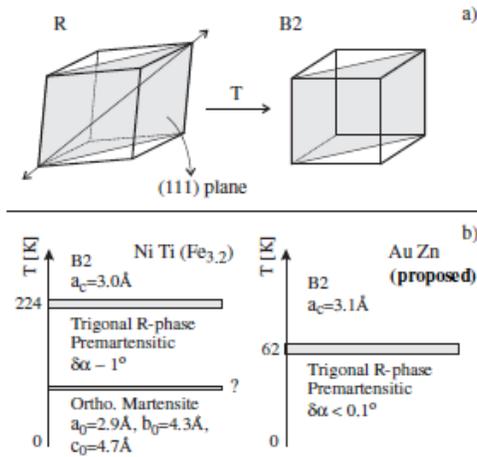


Figure 4. Schematic representation of (a) structural transformation from B2 to R phase and (b) comparison between AuZn and NiTi-Fe_{3.2}.

There is a large similarity between the phase transition in AuZn and that observed in NiTi-Fe_x [5,6]. Figure 4 shows a schematic representation of the phase transition. In Fig. 4a the B2 phase is cubic and the R phase is obtained by effectively pulling along a [111] body diagonal. This causes a distortion and the angle between the cubic axis changes from 90° to 90- α °. If α is large enough the $(1,1,0)$ Bragg peak will split as mentioned above. This occurs in NiTi-Fe_x for $x < 6$ at. %. For $x \geq 6$ at. % no change in lattice parameter is observed and the transition appears continuous, precisely the behavior observed in Au_xZn_{1-x} for $x=50$. It is likely that $\alpha < 0.1^\circ$ and shows up as a broadening of the Bragg peak rather than to a splitting. The comparison also extends to the presence of the q_1 type satellites observed in NiTi-Fe_{3.2} in a detailed x-ray experiment [7]. In Ref. [7] study an incommensurability was observed for both q_0 and q_1 satellites but the incommensurability varied with the Brillouin zone measured. This precludes a simple condensed charge density and/or lattice-wave description of the transformation. Our experiments show similar features for $Au_{50}Zn_{50}$.

Based upon the comparison with NiTi-Fe_x our picture of the transition in AuZn is that the low temperature phase is trigonal or rhombohedral with a very small distortion. It is similar to the R phase of NiTi-Fe_{3.2} and can be considered as a premartensite phase (PM) where the martensite phase is

suppressed. Also, like NiTi-Fe there are phonon anomalies [8] around the q_0 position [2,4] in the cubic parent phase that are precursors to the transformation to the PM phase.

More data are desired to probe the incommensurability of the low temperature phase and to explore in more detail the lattice dynamics of this interesting system.

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