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Structure Determination of the ζ_2' Martensite and the Mechanism of $\beta_2 \rightarrow \zeta_2'$ Transformation in a Au-49.5 at%Cd Alloy

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The crystal structure of the ζ_2' Au-49.5 at%Cd martensite, which has been controversial for 50 years, has been determined by using single crystal data collected by four-circle diffractometer with Mo$K\alpha$ radiation. The space group is P3, trigonal, which has no center of symmetry. This result is in disagreement with that ($P\bar{3}1m$) reported by Vatanayon and Hehemann. The lattice constants are $a=0.8095(3)$ and $c=0.57940(6)$ nm and 18 atoms are present in the unit cell. The structure was refined by the full-matrix least-squares method to a final R factor of 7.8% ($wR=4.1\%$). The transformation mechanism is also discussed and it is shown that the ζ_2' martensite is created by three $\langle 011 \rangle \langle 0\bar{1}1 \rangle$ transverse displacement waves introduced simultaneously. Simulations with displacement waves were also made and a satisfactory results was obtained.

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I. Introduction

The Au-47.5 at%Cd alloy is well-known among many alloys exhibiting martensitic transformations, since the shape memory effect[1] and the unique rubber-like behavior[2] were first found in this alloy. It is also well-known as one of the prototypes, for which the phenomenological crystallographic theory was successfully applied[3]. The parent and martensitic phases are called β_2 (B_2) and γ_2' phases, respectively. The structure of the γ_2' phase was determined to be orthorhombic (2H) by Ölander[4] and recently refined by Ohba *et al.*[5] Thus, except for the rubber-like behavior in the γ_2' martensite, the crystal structure of the martensite, the crystallography of the $\beta_2 \rightarrow \gamma_2'$ transformation[3][6], shape memory effect and superelasticity etc.[7][8], are all well established.

In the Au-Cd alloy system, a slight change in composition (i.e. Au-48.5 ~ 50.0 at%Cd alloys) introduces quite a different martensitic transformation called the $\beta_2 \rightarrow \zeta_2'$ transformation, which is characterized by a very small temperature hysteresis (2 ~ 4 K). The transformation was first studied by Chen[9] in 1954, but even the crystal structure of the ζ_2' martensite is not established yet as discussed in the following, and the crystallography of the $\beta_2 \rightarrow \zeta_2'$ transformation is not established either. Ledbetter and Wayman[10] analyzed the crystallography of the transformation by introducing twinning as a lattice invariant shear, while Tadaki *et al.*[11] claimed that there is no lattice invariant shear in the martensite according to their electron microscopy study. Several interesting phenomena are also associated with the ζ_2' phase. Miura *et al.*[7][8], found a superelasticity in the martensitic phase region, which is associated with the stress-induced $\zeta_2' \rightleftarrows \beta_s'$, (orthorhombic which they claim.) transformation. Morii *et al.*[12] found the shape memory effect and superelasticity associated with $\beta_2 \rightleftarrows \zeta_2'$ transformation recently. Noda *et al.*[13] found a premartensitic behavior from B2 to an incommensurate phase prior to the $\beta_2 \rightleftarrows \zeta_2'$ martensitic transformation. Furthermore, the following complicated phenomena are also known for a long time[14]. Even Au-47.5 at%Cd alloy transforms from β_2 to ζ_2' when a specimen is rapidly cooled after solution treatment†, although the same specimen transforms from β_2 to γ_2' when the specimen is slowly cooled after solution treatment. In order to understand all the behavior, we have to know the structure of the ζ_2' martensite.

The ζ_2' phase of Au-50.0 at%Cd alloy was first found by Köster and Schneider[16] unknowingly in 1940, who did not know the presence of two phases, i.e. γ_2' and ζ_2' in near-equi atomic Au-Cd alloy systems. They reported the structure as bct with $c/a=0.88$. After their report, various structures were proposed, but they did not converge. These studies were critically reviewed by Ledbetter and Wayman[17]. Wilkens[18][19] was the first to have reported that the structure was the rhombohedrally distorted B2 structure with the rhombohedral angle α of 89.6°, $c/a=0.715$ and the unit cell having 18 atoms. The rhombohedral distortion occurs along $\langle 111 \rangle_{B2}$ axis of the B2 parent phase. Ledbetter and Wayman[17] later came to the same conclusion after careful experiment by powder diffraction method and critical reviewing of the previous

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† According to a recent study by Suzuki *et al.*[15], a specimen transforms from β_2 to the mixture of γ_2' and ζ_2'.