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PRECURSOR PHENOMENON OF MARTENSITIC TRANSFORMATION IN Au-49.5at%Cd ALLOY

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ABSTRACT

Phonon softening was observed in the parent phase of a AuCd alloy which transforms from the β_2(B2) parent to ζ_2' (trigonal) martensite. Since Cd strongly absorbs neutrons, the isotope ^{114}Cd was used in preparing the single crystal for the measurements. The $[\zeta\zeta 0]TA_2$ phonon branch was measured and found to be anomalously low. A minimum is present at ζ=0.35 which softens with decreasing temperature towards Ms. The results are consistent with the model proposed by Ohba et al. based upon a crystallographic study of the ζ_2' phase.

INTRODUCTION

Martensitic transformations are becoming more important because the martensitic transformations were found in various materials, such as ceramics or high Tc superconducting materials. One of the most interesting phenomena associated with martensitic transformation is the shape memory effect and superelasiticity effect, which have many applications in electric, automotive, medical fields etc. From view point of the phase transformation, the martensitic transformation is the typical first-order diffusionless transformation, which is the central issue in the recent research.

The relation between phonon softening and the martensitic transformation has been studied for many years especially from view point of observing premartensitc behavior[1,2,3,4]

Au_xCd_{1-x} is one of the alloys, which attracted most the attention of researchers. Near x=0.5 the high temperature structure is well known to be CsCl type. In the low temperature martensite phase, there are two different phases called γ_2' and ζ_2' phase. The structure of γ_2' martensite was determined by Ölander[5] by X-ray powder diffraction, and then reexamined by Tadaki and Shimizu using electron diffraction.[6] The more accurate structure determination of γ_2' phase was made by Ohba et al.[7] using martensite single crystals. The ζ_2' phase appears near x=0.5 and was found in 1940[8] and various structures were proposed by different researchers.[9,10,11] However the crystal structure of the ζ_2' phase was not solved for more than fifty years because of the difficulty in getting a single crystal of the martensite. Recently, the crystal structure of the ζ_2' phase was successfully determined by X-ray diffraction using single crystals of the ζ_2' martensite made by stress induced technique.[12]

From the results of the structure determination of ζ_2' martensite, the transformation mechanism was proposed.[12] The $\zeta 2'$ phase was obtained by applying three <110><1$\bar{1}$0> transverse displacement waves and their higher harmonics. {110} planes were shifted every three layers. Then, phonon softening was expected at ζ=1/3 in the parent phase for forming ζ_2' martensite.

Inelastic neutron scattering technique is the only method to observe the phonon softening at finite wave vectors. However, Au, and especially Cd, have a large neutron absorption coefficient which makes an experiment nearly impossible. By use of the isotope ^{114}Cd, the absorption

coefficient is reduced by a factor of 1/2000 and the difficulty of absorption was overcome.

EXPERIMENTAL

The single crystal was grown from 99.99%Au and 99.5%Cd by the Bridgman method. The isotope ^{114}Cd was provided by Advanced Materials Tech. The composition was $Au_{50.5}Cd_{49.5}$ and the size of the sample was approximately 5 mm in diameter and 50 mm long with the [001] direction along the long axis. The lattice parameter at T=400K is a=0.331 nm and the sample mosaic is uniform and less than 10'. The martensite start and finish temperatures (Ms, Mf) were 304 K and the reverse transformation start (As) and finish (Af) temperatures 308 and 316 K, respectively. These temperatures were determined by measuring the intensity of the 110 reflection of the parent phase. The sample was placed in an aluminum can filled with He gas and attached to the cold finger of a closed-cycle refrigerator. The neutron experiments were performed at H4M spectrometer at the High Flux Beam Reactor located at Brookhaven National Laboratory. Pyrolytic graphite crystals were used for the monochrometer and analyzer and a filter in the scattered beam. The fixed final energy of the neutrons was 14.7 meV. Collimators used for most of the experiments were 40' through the spectrometer.

The $[\zeta\zeta 0]TA_2$ phonon branch in the parent phase was measured. This phonon branch corresponds to shear of the closed packed {110} planes along <110>. In the limit of ζ->0 the slope corresponds to the elastic constant $C'=(C_{11}-C_{12})/2$.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of scattered neutrons measured at ζ=0.35 for four different temperatures. Least squares fitting of the peaks with polynomial was done and shown in the figure simultaneously. The peak position, which is 1.4 meV at 425 K, shifts toward lower energy with decreasing temperature. At 306 K, just above Ms, the peak has shifted to 0.8 meV.

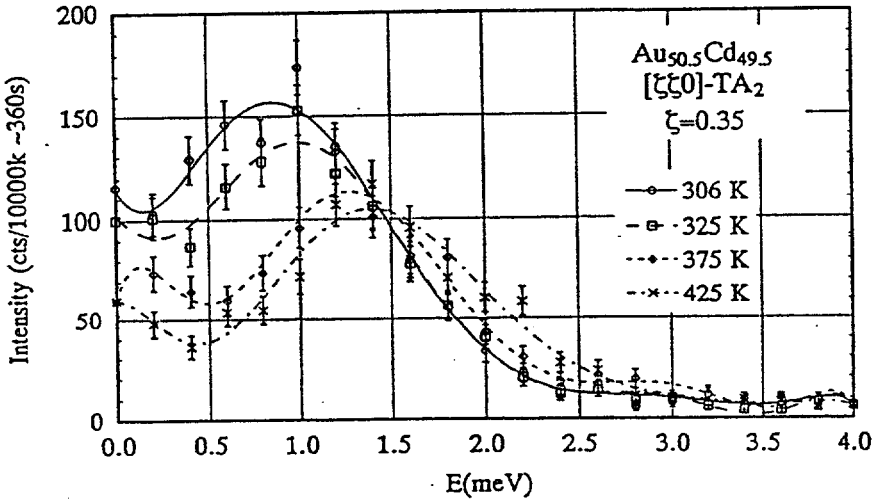

Fig.1. Inelastic neutron scattering spectra at various temperatures measured at Q=(1.35, 0.65,0).

The phonon dispersion curves of the other [ζζ0] LA and TA branches are shown in Fig. 2. The low lying TA_2 branch at various temperatures is shown as well as LA and TA_1 branches measured at 310 K. Comparing with other martensitic materials, the phonon energies of $[\zeta\zeta 0]TA_2$ branch is very low and remains low through the Brillouin zone. The anisotropy of

the two TA branches is defined as the ratio of elastic constants $A=2C_{44}/(C_{11}-C_{12})$, which increases with decreasing temperature toward Ms. Our results of A=12.0 at T=400K and A=14.2 at 310K are within 15% of these obtained from the ultrasonic studies of Zirinsky.[13] In Fig. 3, low energy region of the $[\zeta\zeta 0]TA_2$ branch is enlarged and the temperature dependence of this branch is shown clearly. Precise measurements around ζ=1/3 reveals that the dip appears at ζ=0.35 instead of 1/3. The dip at ζ=0.35 is present even at 425K and it becomes deeper upon approaching the transformation temperature as shown in Fig. 3. The dip at ζ=0.35 which is close to 1/3 seems to be consistent with the proposed transformation mechanism of the ζ_2' martensite.

The similar tendency was reported by Shapiro et al. in NiAl alloy[14]. They measured the phonon dispersion relation in NiAl,[14] which transforms from B2 parent phase to a low temperature phase with structure called 7M(14M)*, and showed a large amount of phonon softening at ζ=1/6 instead of ζ=1/7 which is expected from the structure of martensite. The deviation from ζ=1/3 in AuCd alloy may be discussed in the same way as that discussed for 7M(14M) martensite in a NiAl alloy, i.e. by the wave-vector dependence of the Landau coefficients appearing in the free energy expansion.[15]

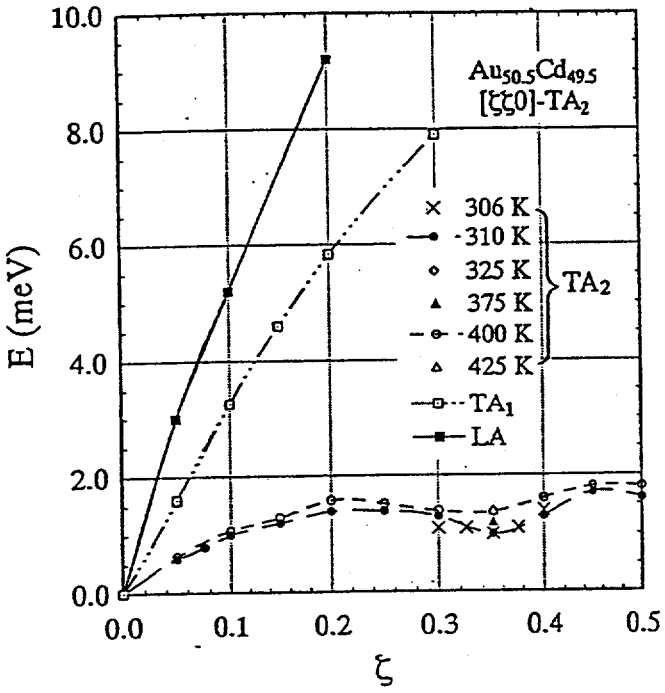

Fig. 2. Phonon dispersion relation of $[\zeta\zeta 0]TA_2$, $[\zeta\zeta 0]TA_1$ and $[\zeta\zeta 0]$LA branch.

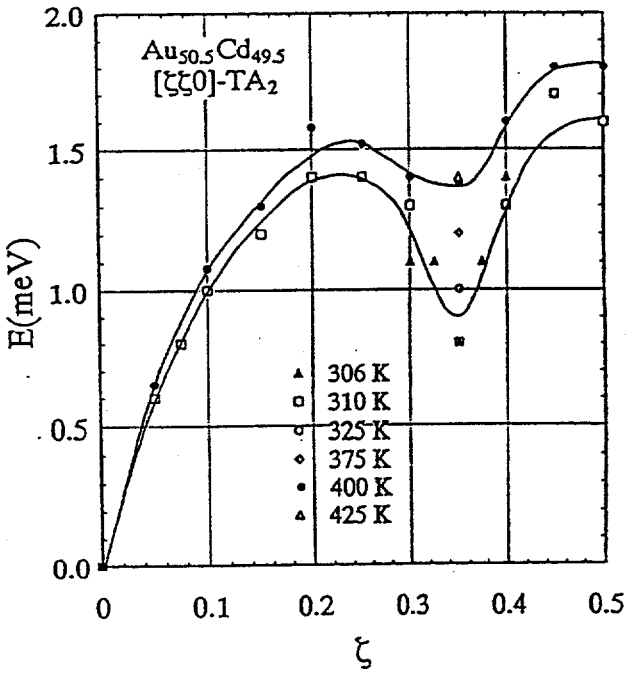

Fig. 3. Phonon dispersion relation of $[\zeta\zeta 0]TA_2$ branch at various temperatures.

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* A new nomenclature is described in a bracket. See Ref (19) for details.

Temperature dependence of the square of the phonon energy at ζ=0.35 is shown in Fig. 4 which is linear with temperature and extrapolates to zero at T_0=250K, which is more than 50K below Ms. Since the martensitic transformation is the first-order diffusionless transformation, the transformation occurs before the phonon energy becomes zero.

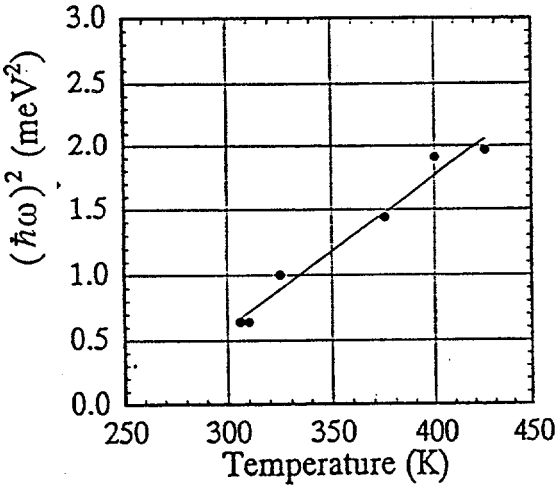

Fig. 4. $(h\omega)^2$ vs. T plot for $[\zeta\zeta 0]TA_2$ branch at z=0.35.

Figure 5 shows a plot of the phonon energy measured along the [110] direction from the reciprocal point of 1.35 0.65 0 where the phonon energy is minimum. The phonon energy along a perpendicular $[\zeta\zeta 0]$ direction was reported in NiAl by Shapiro et al.[13] Although the anomaly of AuCd in phonon dispersion curve is restricted to a valley along [110] as well as NiAl, the valley is wider than that of NiAl.

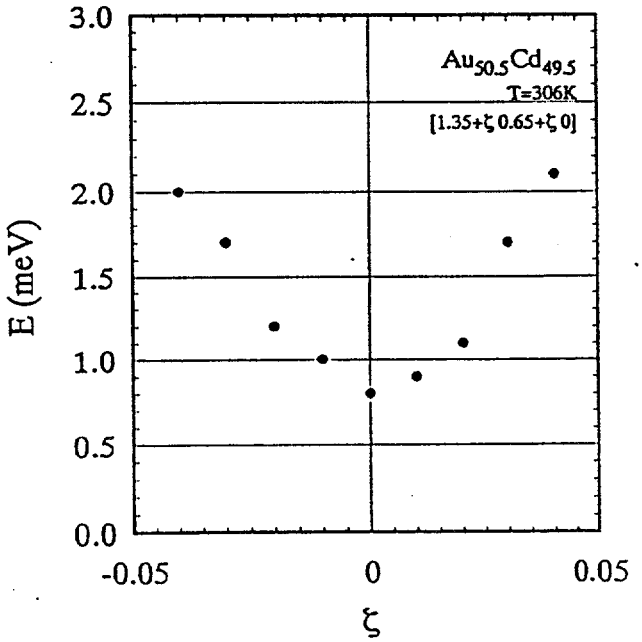

Fig. 5. Phonon energy along a perpendicular $[\zeta\zeta 0]$ direction

The phonon dispersion curve in TiNi was measured by several researchers[16,17,18] who observed a significant softening in the parent phase. The phonon anomaly in the same $[\zeta\zeta 0]TA_2$ branch occurs at ζ=1/3 which is similar to the present case. Although the structure of the TiNi

R phase has not been solved yet, the phonon behavior seems to suggest that the structure of the R phase is the same as $\zeta 2'$ martensite[12].

Several martensitic materials studied[1,2,3,4] reveal a phonon softening at ζ=2/3[110] which is very weak and does not directly relate to the martensitic structure. On the other hand, softening in AuCd, NiAl and TiNi where the anomalies are pronounced directly relates to the martensite structure.

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