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Third-order elastic constants of bcc Cu-Al-Ni

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We have measured the changes in the ultrasonic wave velocity, induced by the application of uniaxial stresses in a Cu-Al-Ni single crystal. From these measurements, the complete set of third-order elastic constants has been obtained. The comparison of results for Cu-Al-Ni with available data for other Cu-based alloys has shown that all these alloys exhibit similar anharmonic behavior. By using the measured elastic constants in a Landau expansion for elastic phase transitions, we have been able to give an estimation of the value of a fourth-order elastic constants combination. The experiments have also shown that the application of a stress in the [001] direction, reduces the material resistance to a $(110)[1\bar{1}0]$ shear and thus favors the martensitic transition. [S0163-1829(96)10233-2]

I. INTRODUCTION

The investigation of bcc solids which, on lowering the temperature and/or by application of a stress undergo structural transitions towards close-packed structures, has been an issue that has attracted the attention of scientists for many years. A particularly interesting transition that bcc solids may exhibit is the martensitic transformation. It is a first order phase transition, diffusionless, that can be basically described by a shear mechanism.[1]

Bcc solids undergoing martensitic transitions have an anomalous dynamical response of the lattice: they exhibit a low TA[110] phonon branch which is accompanied by a low value of the elastic constant $C'[=(C_{11}-C_{12})/2]$,[2] both softening on approaching the transition.

The softening of the TA[110] branch and that of C' is not complete: neither any of the phonon frequencies or the elastic constant reach zero value at the transition point. This incomplete softening is a result of the first-order character of the transition and has the consequence that the classical soft-mode theory is inadequate to describe this kind of displacive transition. Hence, it is necessary to go beyond the harmonic approximation to understand the dynamics relevant to this transition. In a simple approach the transition is assumed to be purely elastic. For elastic transitions, the Landau expression in terms of the combinations of strain components that are adapted to the different crystal symmetries was detailed by Liakos and Saunders.[3] A quantitative applicability of such a Landau theory to the particular transition of a specific material needs the knowledge of second- and higher-order elastic constants. Of particular interest is the third-order term in the expansion, which determines whether the transition will be first or second order.

Among the systems exhibiting martensitic transformations, Cu-based alloys are of significant interest because of their shape-memory properties.[1] The lattice dynamics of these alloys has been analyzed by means of ultrasonic and neutron-scattering techniques. It has been shown that C' and the TA[110] branch have low values[4–8] that result in a large vibrational entropy which is responsible for the thermodynamical stability of the bcc phase.[9] There is incomplete softening as the temperature approaches the transition point. An important result related to this incomplete softening is that the elastic anisotropy evaluated at the transition point has a fixed value, independent of the alloy system and of the specific composition of the sample.[7,10]

In spite of the considerable effort in quantifying the vibrational behavior of Cu-based alloys, there are still very few experimental data on the terms higher than second order in the free-energy expansion in terms of the elastic strain. The

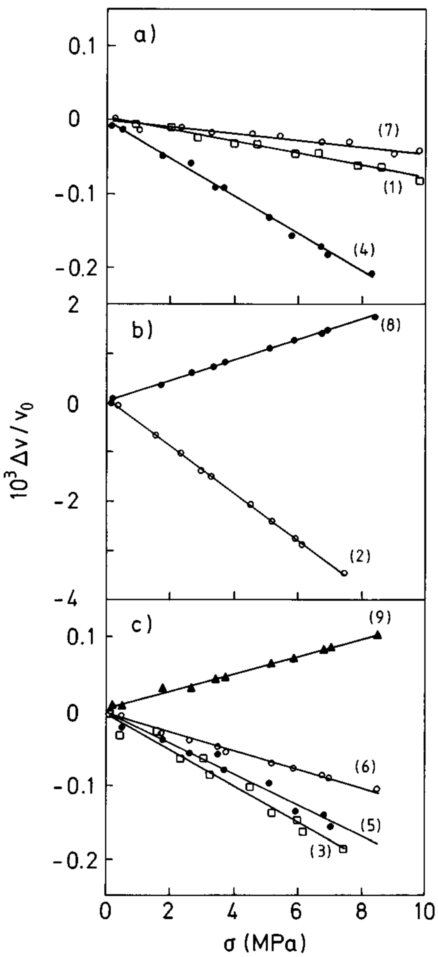

FIG. 1. Relative change in the velocity of ultrasonic waves under the application of a uniaxial stress. (a) longitudinal modes, (b) slow and (c) fast shear modes. Solid lines are linear fits to the data. Curves have been labeled according to Table I. Notice the enlarged scale in (a) and (c).

complete set of third-order elastic constants (TOEC) has only been measured for Cu-Zn-Al (Ref. 11) and Cu-Al-Pd;[12] also, some TOEC combinations have been measured for Cu-Al-Be.[13] In this work we present the complete set of TOEC for Cu-Al-Ni.

II. EXPERIMENTAL DETAILS

The sample was one of the Cu-Al-Ni crystals previously investigated by ultrasonic and neutron-scattering techniques,[4,8] with composition $Cu_{2.726}Al_{1.122}Ni_{0.152}$. From the original rod, a cubic-shaped specimen was cut (about 10-mm side) using a low-speed diamond saw, with faces parallel to the (110), $(1\bar{1}0)$, and (001) planes. The sample was polished flat to surface irregularities of about 2 μm and parallel to better than 10^{-3} rad. To remove stresses caused by the cutting procedure, the sample was annealed for 1 h at 1273 K and quenched into water at 298 K. The nominal transition temperature was 220 K.

To generate and detect the ultrasonic waves we have used 10 MHz quartz transducers. Acoustic coupling between transducer and sample was achieved by using Dow Resin 276-V9. To apply uniaxial stresses we have used a universal tensile machine equipped with compression grips, working in its compressive mode. A reinforced stainless-steel plate was mounted at the bottom of the upper compression grip, with a spherical stainless-steel ball between the plate and the surface of the grip; this mounting minimized any possible shear component of the applied stress, thus ensuring that once the specimen was sandwiched between this plate and the lower grip, it was subjected to truly uniaxial stresses.

TABLE I. Slope of the $\Delta v/v_0$ versus σ curves for ultrasonic waves propagating with **N** and **U** as propagation and polarization vectors, respectively, and for a uniaxial stress applied along the **M** direction.

Mode	**N**	**U**	**M**	$\frac{\partial \Delta v/v_0}{\partial \sigma}$ (10^{-10} Pa^{-1})
1	$[1\bar{1}0]$	$[1\bar{1}0]$	[001]	-0.07 ± 0.01
2	[110]	$[1\bar{1}0]$	[001]	$-4.7\ \pm0.8$
3	[110]	[001]	[001]	-0.25 ± 0.04
4	[001]	[001]	$[1\bar{1}0]$	-0.26 ± 0.01
5	[001]	[110]	[110]	-0.18 ± 0.03
6	[001]	$[1\bar{1}0]$	[110]	-0.13 ± 0.02
7	$[1\bar{1}0]$	$[1\bar{1}0]$	[110]	-0.03 ± 0.02
8	$[1\bar{1}0]$	[110]	[110]	$2.2\ \pm0.5$
9	$[1\bar{1}0]$	[001]	[110]	0.10 ± 0.02

Changes in the ultrasonic wave velocity were measured by using the phase-sensitive detection technique. To avoid the requirement for determination of changes induced in sample dimensions, we have used the ''natural velocity'' technique.[14]

Since the changes in the transit time induced by uniaxial stresses are very small, it is important to have an accurate control of the temperature. For this reason, although during the time of measurement possible drifts of the temperature did not exceed ±0.3 K, a thermocouple was attached to the specimen so that the temperature was continuously monitored; this enabled us to correct the data (when necessary) from possible temperature drifts. The whole system was computer controlled via GPIB, and transit time, uniaxial load, and specimen temperature were simultaneously acquired.

TABLE II. Second- and third-order elastic constants for different Cu-based alloys.

	Cu-Al-Ni	Cu-Zn-Al	Cu-Al-Pd
C_L (GPa)	230.0	193.7	228.5
C'(GPa)	7.42	7.06	7.76
C_{44} (GPa)	97.7	84.4	91.4
C_{111} (TPa)	-1.79 ± 0.15	-2.08	-1.78
C_{112} (TPa)	-1.05 ± 0.15	-1.06	-0.78
C_{123} (TPa)	-0.98 ± 0.10	-0.92	-0.94
C_{144} (TPa)	-0.93 ± 0.10	-1.02	-0.94
C_{166} (TPa)	-1.08 ± 0.10	-1.02	-0.93
C_{456} (TPa)	-0.60 ± 0.30	-0.66	-0.63
Reference		11	12

III. THE THIRD-ORDER ELASTIC CONSTANTS

TOEC can be obtained from the changes in the ultrasonic velocity caused by uniaxial stresses.[14] Figure 1 shows an example of the measured dependence of the ultrasonic velocities with the applied stress. Curves are labeled according to the wave propagation and polarization directions and to the direction of the applied stress, as indicated in Table I. For each curve, data points have been taken during both increasing and decreasing pressure runs. It is worth noting that usually, both sets of data points fall on a single straight line, but this was not the case in some measurements where the change with stress was very small. This undesirable effect arose from a small temperature drift during the experiment which is difficult to avoid, but, since the temperature of the sample was continuously monitored, it was possible to correct each point for its temperature drift, by using the temperature dependence of the corresponding ultrasonic velocity. After this correction all data points lay on a single straight line. From Fig. 1, it is apparent that the slow shear modes [Fig. 1(b)], associated with the elastic constant C', are the most sensitive to the applied stress.

In Table I we present the values obtained for the stress derivative of the ultrasonic velocity, computed by fitting a straight line to each set of data points. Values given in the table correspond to an average over eight independent runs, four of them with the transducer coupled to one face and the other four with the transducer on the opposite face. The errors are the maximum deviation from the average. The TOEC obtained using these data and values of the SOEC previously published[8] are listed in Table II together with published data for other Cu-based shape memory alloys.[11,12] The values of SOEC and TOEC found for Cu-Al-Ni are similar to those of the other Cu-based alloys. All TOEC are negative, indicating the usual behavior of an increase of the vibrational frequencies under stress, giving rise to an increase of the strain-free energy. The absolute value of TOEC is large, being an indication that Cu-based alloys are considerably anharmonic.

IV. DISCUSSION

We will restrict ourselves to the simpler Landau approach to the martensitic transformation. For a cubic crystal, the free-energy expansion in terms of the symmetry adapted strain tensor combinations reads[3]

$$\phi=\frac{1}{6}(C_{11}+2C_{12})(\eta_0^0)^2+\frac{1}{4}(C_{11}-C_{12})(\eta_1^2+\eta_2^2)+\frac{1}{2}C_{44}(\eta_3^2+\eta_4^2+\eta_5^2)+\frac{1}{54}(C_{111}+6C_{112}+2C_{123})(\eta_0^0)^3$$
$$+\frac{1}{12}(C_{111}-C_{123})\eta_0^0(\eta_1^2+\eta_2^2)+\frac{1}{24\sqrt{3}}(C_{111}-3C_{112}+2C_{123})\eta_1(\eta_1^2-3\eta_2^2)+\frac{1}{6}(C_{144}+2C_{155})\eta_0^0(\eta_3^2+\eta_4^2+\eta_5^2)$$
$$+\frac{1}{4\sqrt{3}}(C_{144}-C_{155})\eta_1(2\eta_5^2-\eta_4^2-\eta_3^2)+\frac{1}{4}(C_{144}-C_{155})\eta_2(\eta_3^2-\eta_4^2)+C_{456}\eta_3\eta_4\eta_5$$
$$+\frac{1}{192}(C_{1111}-4C_{1112}+3C_{1122})(\eta_1^2+\eta_2^2)^2, \quad (1)$$

where η_i are combinations of the Lagrangian strains.[3] Usually, only symmetry-breaking terms are considered in expression (1) to describe the elastic phase transition.

A first result showing up from a Landau analysis is that the martensitic transformation cannot be described only by a $\{110\}\langle 110\rangle$ shear, given by η_2: the absence of a cubic term in η_2 would result (at lower order in the expansion) in a second-order phase transition, in contrast with the marked first-order character of the martensitic transformation.

The following simple approach is to consider the tetragonal distortion η_1, as has been done by Nagasawa and Yoshida[15] in their analysis of Cu-Zn-Al alloys. It is worth mentioning that a tetragonal distortion is very close to a pure Bain strain that brings the bcc structure towards the close-packed fcc. On the other hand the tetragonal distortion can be obtained as the result of two pure perpendicular shears.

By considering η_1 to be the strain order parameter, the first-order character of the phase transition will be governed by the third-order cubic invariant:

$$B\equiv\frac{1}{24\sqrt{3}}(C_{111}-3C_{112}+2C_{123}) \quad (2)$$

which, using the data of Table II amounts to $B=-14.43$ GPa for Cu-Al-Ni. It is worth noticing the negative value of this invariant, which makes a first-order transition possible.

A complete analysis of the elastic phase transition in terms of the Landau description requires knowledge of the FOEC. Unfortunately, they are difficult to obtain experimentally and have only been measured for very few materials. It is however possible to make an estimation of the value of the FOEC combination C appearing in Eq. (1),

$$C\equiv\frac{1}{192}(C_{1111}-4C_{1112}+3C_{1122}), \quad (3)$$

by taking advantage that B, C, and C' are related to the entropy change at the phase transition as follows:[16]

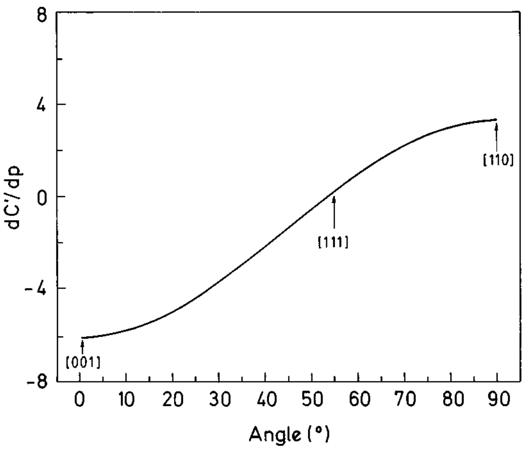

FIG. 2. Stress derivative of the C' elastic constant as a function of the angle between [001] and the uniaxial compression directions.

$$\Delta S = \frac{1}{8\rho}\left(\frac{B^2}{C^2}\right)\frac{dC'}{dT} \tag{4}$$

with ρ being the mass density.

By using $\rho=7.09\times10^3$ kg m^{-3},[17] $dC'/dT=3.14\times10^6$ Pa K^{-1},[8] and $\Delta S=1.5$ J K^{-1} mol^{-1},[7] we have obtained $C\simeq20$ GPa as an estimate of the FOEC combination. It is interesting to notice that although this is a rough estimate, the value obtained is quite similar to the value calculated using the FOEC of pure copper ($C=27$ GPa).[18]

Another interesting point that the present measurements enable us to discuss is the stress dependence of the SOEC. As already mentioned, C' is the most sensitive elastic constant to the applied uniaxial stress. We have computed the value of its stress derivative for stresses applied in different directions, by using the data in Table I and the Thurston and Brugger[14] equation. Results are plotted in Fig. 2 as a function of the angle between the [001] and the uniaxial stress directions. The most significant feature showing up from this figure is the high anisotropy of the stress dependence of C': it changes drastically as the direction of the stress varies. The curve exhibits a minimum when the stress is applied in the [001] direction. That is, the mechanical stability of the bcc lattice is lower when stressed on the [001] direction. Also, similar findings have been reported for Cu-Zn-Al.[19] According to this reduction in mechanical stability, it is expected that for Cu-Al-Ni, the critical stress (the stress needed to transform to martensite) will be lower when applied on the [001] direction as has been shown to occur in Cu-Zn-Al.[19]

Concerning the effect of a [001] stress, it is worthwhile to remember that in order to transform the bcc (110) planes into the corresponding close-packed basal planes of the martensitic structure, a compression on the [001] direction is needed; this compression changes the bonding angle from 109.47° to 120°.[20] Therefore, the application of an external [001] stress, will help this mechanism.

In summary, this paper presents measurements of the complete set of TOEC for Cu-Al-Ni at room temperature, which provide quantitative data for the anharmonicity of this shape-memory alloy. It has been shown that the TOEC play a relevant role in describing the instability of the bcc structure towards the martensitic transformation.

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