Elastic constants of bcc Cu-Al-Ni alloys

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(Received 7 December 1993)

We have measured the adiabatic elastic constants of two Cu-Al-Ni martensitic alloys using ultrasonic methods and we have compared the results to recent neutron-scattering experiments. It is shown that the elastic behavior of Cu-Al-Ni alloys follows the same trends exhibited by other Cu-based alloys; in particular, the TA2 long-wavelength acoustic modes are softer than all other modes.

I. INTRODUCTION

The stability of the bcc structure exhibited by a number of metals and alloys has been the subject of continuous interest for many years.[1-3] Since the pioneer work of Zener[1] it has been acknowledged that a large entropy is the stabilizing factor for the bcc phase, since close-packed phases have lower energies. This large entropy has mostly a vibrational origin[4,5] and is associated with a low transverse acoustic TA2 branch, and a low value of the elastic constant $C' = (C_{11} - C_{12})/2$.

On cooling, many of these bcc metals and alloys undergo a phase transition towards a close-packed structure. The transformation is first order, diffusionless, and is principally described by a shear; it is the martensitic transformation.[6] Typical examples of materials undergoing these transitions can be found in alkali metals, transition metals, and many noble-metal-based alloys. Among them, the Cu-based alloys have received special interest because of their technologically important shape-memory properties, associated with the martensitic transformation.[7]

In the last few years, considerable effort has been devoted towards an understanding of the martensitic transformation. Several Landau-type models have been proposed[8,9] that involve two coupled order parameters: a uniform strain and a phonon mode (shuffle). Also, computer simulation studies qualitatively describe the vibrational properties of bcc solids.[10] The development of these models has renewed the effort to determine the vibrational and elastic properties of materials undergoing martensitic transformations.

In this paper we present experimental results on the elastic behavior of Cu-Al-Ni single crystals just above their transition temperatures M_s. The data reported here complement a previous neutron-scattering study of the vibrational behavior of several Cu-based bcc alloys.[11]

II. EXPERIMENTAL

Two Cu-Al-Ni single crystals with compositions $Cu_{2.742}Al_{1.105}Ni_{0.152}$ and $Cu_{2.726}Al_{1.122}Ni_{0.152}$ were

prepared from 99.99% pure Cu and Ni and 99.999% pure Al. Crystal growth was accomplished using the modified Bridgman technique in pointed alumina crucibles at a growth rate of approximately 1.5 μm/sec. Following crystal growth, the boules were cleaned with dilute nitric acid, heat treated at 1273 K for 24 h, and quenched into water at 298 K.

Samples for elastic-constant measurements were cut into a cubic shape (about 10-mm side) using a low-speed diamond saw, with faces parallel to the (110), (1$\bar{1}$0), and (001) planes. The samples were polished flat to surface irregularities of about 2 μm and parallel to better than 10^{-3} rad. To remove stresses caused by the cutting process, samples were annealed for one hour at 1273 K and quenched into water at 298 K. The nominal transition temperatures were 260 and 220 K for $Cu_{2.742}Al_{1.105}Ni_{0.152}$ and $Cu_{2.726}Al_{1.122}Ni_{0.152}$ respectively.

Elastic constants were determined using a pulse-echo ultrasonic method. Both X-cut and Y-cut transducers were used to generate and detect 10-MHz ultrasonic pulses. Acoustic coupling between sample and transducer is optimized using Dow resin 276-V9 and Nonaq stopcock grease in the temperature ranges 210–350 and 77–270 K, respectively. Ultrasonic-pulse transit times were obtained using the phase-sensitive detection technique (MATEC, MBS-8000).[12]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The velocity of ultrasonic waves has been measured along the [110] direction of the samples. The adiabatic second-order elastic constants at room temperature for the two crystals investigated are shown in Table I. The values correspond to an average over three independent runs, and the error is the maximum deviation from the mean value. We have double-checked the consistency of our data by measuring the velocity of ultrasonic waves along the [100] direction. From these measurements we have obtained $C_{44} = 98.0$ GPa, $C_{11} = 137$ GPa for $Cu_{2.726}Al_{1.122}Ni_{0.152}$ and $C_{44} = 96.3$ GPa, $C_{11} = 136$ GPa for $Cu_{2.742}Al_{1.105}Ni_{0.152}$. These values are within 4% scatter coincident with those obtained from the data

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TABLE I. Elastic constants C_{IJ} at room temperature, their relative thermal variation $\Gamma_{IJ} = C_{IJ}^{-1} dC_{IJ}/dT$, and C' at the transition temperature M_s.

	C_L (GPa)	C_{44} (GPa)	C' (GPa)	$10^4 \Gamma_L$	$10^4 \Gamma_{44}$	$10^4 \Gamma'$	$C'(M_s)$ (GPa)
$Cu_{2.742}Al_{1.105}Ni_{0.152}$	225	95	7.34	-2.31	-3.63	4.36	7.22
	(± 5)	(± 3)	(± 0.06)	(± 0.14)	(± 0.02)	(± 0.09)	
$Cu_{2.726}Al_{1.122}Ni_{0.152}$	230	95	7.48	-2.54	-3.83	4.25	7.23
	(± 9)	$(\pm 3).$	(± 0.05)	(± 0.08)	(± 0.06)	(± 0.08)	

presented in Table I $(C_{11} = C_L + C' - C_{44})$. It must be mentioned that the present values for C_{11} and C_{44} are very close to the ones reported by Hausch and Török[13] for $Cu_{2.744}Al_{1.104}Ni_{0.148}$, but they reported $C'=9.4$ GPa, which is larger than our values.

We have also measured the temperature dependence of the elastic constants close to the nominal martensitic transformation temperature, M_s. Below M_s, the surface relief associated with the appearance of the martensitic domains breaks the acoustic coupling between the sample and transducer, causing the ultrasonic echoes to disappear. In Fig. 1 we have plotted typical examples for the relative change of the elastic constants with temperature, for the two samples investigated. No anomalous behavior is found for C_L and C_{44}: they increase as the temperature is reduced. C' decreases as the temperature drops; that is, the material becomes softer for a (110) $\langle 1\bar{1}0 \rangle$ shear. This behavior is common for all noble-metal alloys undergoing martensitic transformations.[14] The decrease in C' when the temperature is reduced has been found to be linear, and the corresponding slopes are listed in Table I.

It is worth stressing that ultrasonic velocities could not be measured down to the nominal M_s. Several degrees above M_s a marked increase in echo attenuation occurred, accompanied by a change in slope in the curve of elastic constant versus temperature. To investigate the origin of these anomalies we have performed high-sensitivity calorimetry on the same samples used for ultrasonic measurements. A magnified view of the temperature range just above M_s is shown in Fig. 2 for $Cu_{2.726}Al_{1.122}Ni_{0.152}$; the inset shows the complete thermogram. It is clear that the beginning of the anomalous behavior in C' (marked with an arrow in Fig. 1) coincides with the first thermal effect detected calorimetrically, corresponding to the transformation of a small amount of material. The occurrence of transformation of a small fraction (less than 1%) of the sample above M_s is a typical feature in bulky samples subjected to a quench. Internal stresses are generated during the quench, that are retained in the sample and locally increase the transition temperature. A detailed study of this effect has already been reported on Cu-Zn-Al by one of us.[15]

It is instructive to compare the elastic behavior of Cu-Al-Ni with the behavior of other Cu-based martensitic alloys. All the elastic constants and their temperature dependence are very similar to the values previously reported for Cu-Al-Pd,[16] and Cu-Al-Be.[17] It is of special
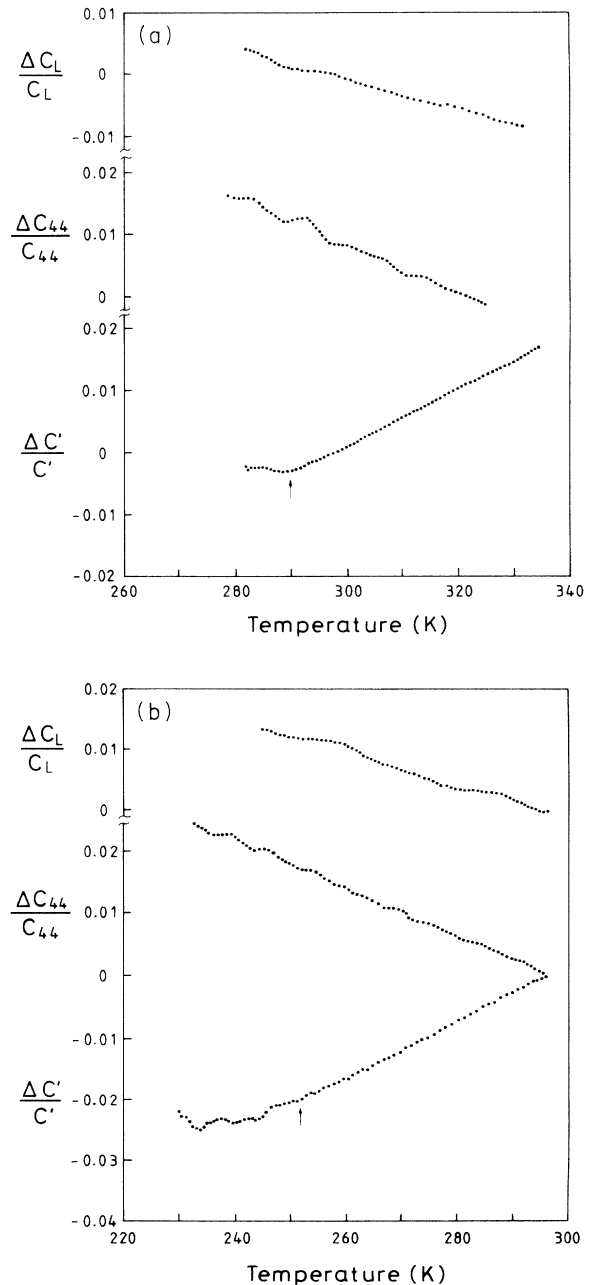

FIG. 1. Typical examples for the relative change of the elastic constants with temperature for (a) $Cu_{2.742}Al_{1.105}Ni_{0.152}$ and (b) $Cu_{2.726}Al_{1.122}Ni_{0.152}$.
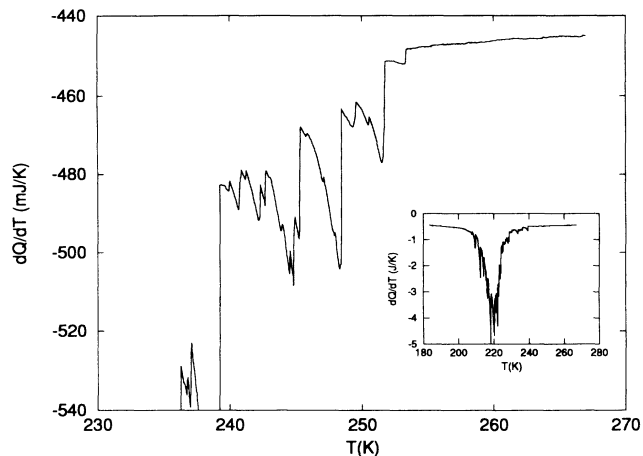
FIG. 2. Enlarged view of the thermal curve close to the transition temperature for $Cu_{2.726}Al_{1.122}Ni_{0.152}$. The inset shows the complete thermal curve.

Reduced wave vector

FIG. 3. TA2 phonon dispersion curves at room temperature for (a) $Cu_{2.742}Al_{1.105}Ni_{0.152}$, (b) $Cu_{2.726}Al_{1.122}Ni_{0.152}$, (c) $Cu_{2.963}Al_{0.925}Be_{0.112}$ (Ref. 11), (d) $Cu_{2.70}Al_{1.08}Pd_{0.22}$ (Ref. 16), (e) $Cu_{2.71}Zn_{0.77}Al_{0.52}$ (Ref. 19), and (f) $Au_{0.92}Cu_{1.20}Zn_{1.88}$ (Ref. 20). The lines are the slopes at the origin computed using the values of C' measured ultrasonically.

interest to evaluate C' at M_s. Values are given in Table I. They coincide (within 3% error) with the values found for Cu-Al-Be and Cu-Zn-Al.[17] Indeed, the present results for Cu-Al-Ni confirm our previous findings that C' at the transition temperature always takes similar values. A phenomenological explanation for this will be given elsewhere.[18]

We finally compare present values of C' with inelastic neutron-scattering experiments carried out on the same crystals, performed at the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory. We have used a 20' collimator in order to be able to measure at low wave vectors. In Figs. 3(a) and 3(b) we present the origin of the TA2 branch for the two crystals investigated. The straight line is the slope at the origin computed using the values of C' given in Table I. A striking feature is that these slopes are lower than the ones obtained by extrapolation to zero frequency of the TA2 branch. To check whether this is a common feature for martensitic alloys, we have collected data for the TA2 branch and C' from the literature[11,16,19,20] and have replotted them on the same scales in Figs. 3(c)–3(f). Although in most cases no neutron data exist for $q < 0.2$ it is clear that, within the combined experimental errors from neutron and ul-
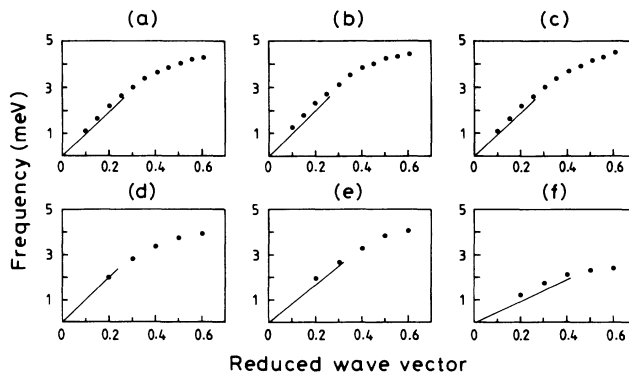
trasound experiments, the slope computed from C' is always lower than the extrapolation of the phonon branch to $q = 0$. These results show that the long-wavelength transverse acoustic modes are softer than all other modes. Anharmonic effects could be the source of this extra softening. Nevertheless, to our knowledge there is still no theoretical justification for this fact.

To conclude, we have measured the elastic constants of Cu-Al-Ni and their temperature dependence down to the martensitic transformation temperature. We have found that this alloy behaves similarly to other Cu-based martensitic alloys. A comparison of phonon dispersion curves and ultrasonic measurements for a number of noble-metal-based alloys suggests that the long-wavelength acoustic TA2 modes are softer than all other modes.

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