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Lattice-dynamical study of the premartensitic state of the Cu-Al-Be alloys

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Neutron-scattering techniques have been used to study the premartensitic state of a family of Cu-Al-Be alloys, which transform from the bcc phase to an 18R martensitic structure. We find that the phonon modes of the $TA_2[110]$ branch have very low energies with anomalous temperature dependence. A slight anomaly at $q=\frac{2}{3}$ was observed; this anomaly, however, does not change significantly with temperature. No elastic peaks, related to the martensite structure, were found in the premartensitic state of these alloys. The results are compared with measurements, performed under the same instrumental conditions, on two Cu-Al-Ni and a Cu-Zn-Al martensitic alloy.

I. INTRODUCTION

Many bcc metals and alloys undergo phase transitions to close-packed-layer structures, such as fcc and hcp, or the ω phase.[1,2] In all of these transformations, the atomic displacements include phonon modes of the TA[110] and/or TA[112] branches. The ω phase, for instance, can be considered as arising from the condensation of the TA $\frac{1}{3}(211)$, or equivalently the LA$\frac{2}{3}(111)$ phonon mode; the transformation to the $9R$ (or $18R$) and the $2H$ structure, on the other hand, involves the $q=\frac{2}{3}$ and the zone-boundary phonon of the TA[110] branch, respectively. Examples of such transformations[1-4] can be found in the alkali metals, group-III and group-IV transition metals and a large number of alloys.

The transformations occurring in copper-based alloys have been the subject of numerous theoretical and experimental investigations[1,2,5] because of the technological importance of their shape-memory properties. Particular attention has been directed toward an understanding of premonitory effects of the transition in the premartensitic phase of these alloys. Such precursor effects include anomalies in the phonon-dispersion curves and elastic constants as well as the observation of elastic or diffuse diffraction peaks related to the martensite structure.

In Cu-based alloys the bcc phase is stable at high temperatures, but the range of solid solution decreases with decreasing temperature. As a result, the bcc phase usually decomposes below temperatures of the order of 400–500 °C. For most Cu-based alloys, however, by rapidly cooling to room temperature the bcc phase can be retained and becomes ordered before the martensitic transformation occurs.

In the present paper, we present the results of a lattice-dynamical study by neutron scattering of a series of Cu-Al-Be alloys which transform to an $18R$ structure. The results are compared with measurements, under the same instrumental conditions, on two Cu-Al-Ni and a Cu-Zn-Al alloys.

II. EXPERIMENT

The Cu-Al-Be and Cu-Zn-Al crystals used in these experiments were provided to us by Morin and Belkahla of the Institut National des Sciences Appliquées, France. Cu-Al-Be alloys were obtained by adding appropriate quantities of 99.99 wt % pure Cu and Al to a Cu-4.3 wt % Be alloy. Cu-Zn-Al alloys were prepared from 99.99 wt % pure elements. Single crystals of these alloys were grown in quartz crucibles by the Bridgman technique. The crystals were homogenized in air at 1120 K and then quenched into water at 298 K. Following this treatment the crystals were cleaned with dilute nitric acid.

The alloys for the Cu-Al-Ni system were prepared in the Ames Laboratory from 99.99 wt % Cu and Ni and 99.999 wt % pure Al. Appropriate quantities of the pure metals were cleaned and arc-melted under argon into 50 gram buttons. The buttons were then melted together and drop cast into a cylindrical copper mold. Crystal growth was accomplished using the modified Bridgman technique in pointed alumina crucibles at a growth rate of approximately 1.5 μm/s. Crystals up to 25.4 mm in diameter and 60 mm in length were prepared. Following crystal growth, the boules were cleaned with dilute nitric acid, encapsulated in a quartz tube under argon, heat treated at 1273 K for 24 h, and quenched into water at 298 K.

The single crystals studied in this work, together with their composition and calorimetrically measured[6-8] transition temperatures, are listed in Table I.

The measurements were performed on three triple axis spectrometers (HB-3, HB-2, HB-1A) at the HFIR of the ORNL. All measurements on HB-2 and HB-3 were performed at a constant scattered-neutron energy (most of them at 14.7 meV) and those on HB-1A at a constant incident-neutron energy of 14.7 meV. Most measurements were performed using pyrolytic graphite reflecting from the (002) planes as monochromator and analyzer, and collimation of either 40 or 20 minutes of arc before and after the sample. In all measurements, a pyrolytic

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TABLE I. Crystals used in this work.

Crystal	Composition	Transition temperature (K)
A	$Cu_{2.963}Al_{0.925}Be_{0.112}$	261
B	$Cu_{2.970}Al_{0.914}Be_{0.116}$	227
C	$Cu_{2.959}Al_{0.922}Be_{0.119}$	228
E	$Cu_{2.949}Al_{0.909}Be_{0.142}$	145
1	$Cu_{2.742}Al_{1.105}Ni_{0.152}$	260
2	$Cu_{2.726}Al_{1.122}Ni_{0.152}$	220
	$Cu_{2.664}Zn_{0.756}Al_{0.58}$	168

graphite filter was positioned either before or after the sample to attenuate the higher-order contamination of the neutron beam.

The samples were mounted under He in a sample can, which was attached to the cold finger of a standard closed cycle He refrigerator. To avoid decomposition of the bcc phase, no sample was heated to temperatures higher than 100 °C. No evidence of additional phases was found in the samples examined in this study.

III. EXPERIMENTAL RESULTS AND DISCUSSION

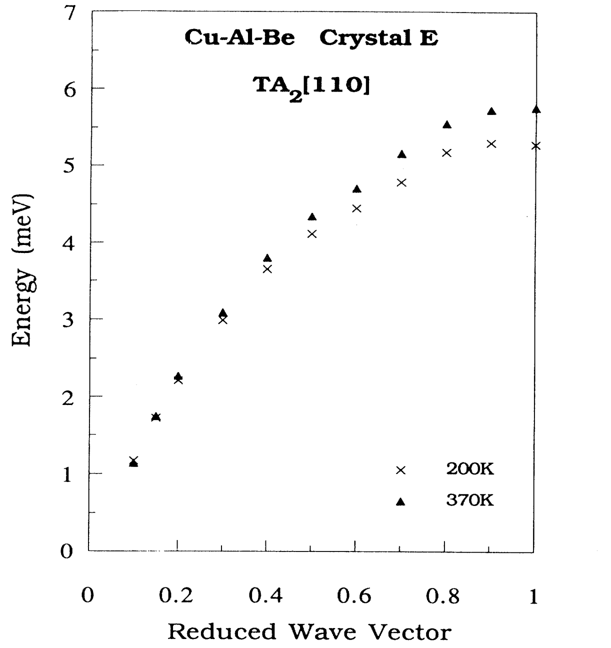

FIG. 1. $TA_2[110]$ phonon-dispersion curve of Cu-Al-Be crystal E at $T=200$ and 370 K.

The temperature dependence of the TA[110] branch with polarization ‖ to the $[1\bar{1}0]$ direction of four Cu-Al-Be alloys, with transition temperatures from 145 to 261 K (see Table I), were measured with the crystals oriented in the (001) scattering plane. The measured energies for the four alloys are tabulated in Table II. The $TA_2[110]$ branch of crystal E, measured at $T=200$ and 370 K, is plotted in Fig. 1. It is seen that the energies of the phonon modes of this branch are very low and reach approximately 5 meV at the zone boundary. The energies decrease with decreasing temperature and a slight saddle point in the vicinity of $q=\frac{2}{3}$ (110) is observed. This slight anomaly, however, does not change significantly with temperature.

The results obtained on the Cu-Al-Be system were compared with measurements performed under the same instrumental conditions on two Cu-Al-Ni alloys. The measured phonon energies of both crystals are tabulated in Table III. The $TA_2[110]$ branch of crystal 2, measured

TABLE II. Measured $TA_2[110]$ phonon energies in meV of four Cu-Al-Be crystals. The composition of the crystals is given in Table I.

Crystal	A		B		C		E	
	T(K)							
q	294	368	270	370	270	370	200	370
0.10	1.11±0.02	1.11±0.01	1.25±0.01	1.25±0.01	1.28±0.02	1.28±0.02	1.17±0.01	1.14±0.01
0.15	1.63±0.01	1.71±0.02	1.73±0.03	1.76±0.02	1.70±0.02	1.71±0.02	1.72±0.02	1.74±0.01
0.20	2.18±0.02	2.22±0.02	2.19±0.02	2.22±0.02	2.20±0.02	2.23±0.02	2.21±0.02	2.27±0.02
0.25	2.60±0.01	2.63±0.02	2.59±0.01	2.64±0.01	2.62±0.02	2.66±0.02		
0.30	3.00±0.01	3.04±0.01	2.99±0.01	3.04±0.01	3.01±0.01	3.06±0.01	2.99±0.02	3.09±0.02
0.35	3.34±0.01	3.40±0.01	3.34±0.01	3.40±0.01	3.36±0.01	3.43±0.01		
0.40	3.65±0.01	3.72±0.02	3.65±0.01	3.72±0.02	3.66±0.02	3.74±0.02	3.65±0.02	3.80±0.02
0.45	3.93±0.02	3.98±0.02	3.89±0.01	3.98±0.02	3.92±0.01	4.02±0.02		
0.50	4.15±0.02	4.25±0.02	4.14±0.01	4.26±0.02	4.16±0.02	4.28±0.02	4.11±0.02	4.34±0.02
0.55	4.31±0.02	4.42±0.03	4.31±0.02	4.45±0.02	4.36±0.02	4.49±0.02		4.56±0.02
0.60	4.49±0.03	4.59±0.02	4.47±0.02	4.66±0.02	4.55±0.02	4.69±0.02	4.45±0.03	4.71±0.02
0.65	4.62±0.02	4.78±0.02	4.64±0.02	4.83±0.02	4.72±0.02	4.91±0.02		4.93±0.02
0.70	4.86±0.02	5.04±0.02	4.84±0.01	5.03±0.02	4.93±0.02	5.13±0.03	4.79±0.02	5.16±0.02
0.75	5.08±0.03	5.21±0.03	5.05±0.02	5.24±0.02	5.16±0.02	5.35±0.03		5.35±0.02
0.80	5.23±0.03	5.44±0.03	5.21±0.02	5.46±0.02	5.32±0.03	5.55±0.02	5.18±0.03	5.55±0.03
0.85	5.36±0.03	5.51±0.03	5.32±0.02	5.55±0.03	5.40±0.02	5.63±0.02		5.63±0.03
0.90	5.35±0.04	5.55±0.03	5.35±0.02	5.55±0.04	5.47±0.04	5.72±0.03	5.30±0.02	5.73±0.04
0.95	5.38±0.03	5.52±0.03	5.36±0.03	5.63±0.04	5.49±0.03	5.76±0.04		
1.00	5.36±0.03	5.54±0.02	5.34±0.03	5.61±0.02	5.49±0.04	5.72±0.04	5.28±0.02	5.76±0.05

TABLE III. Measured $TA_2[110]$ phonon energies in meV of two Cu-Al-NI and a Cu-Zn-Al crystal. The composition of the crystals is given in Table I.

Crystal	1		2		Cu-Zn-Al	
			T(K)			
q	294	373	270	370	200	370
0.10	1.12±0.02	1.11±0.01	1.32±0.02	1.33±0.03	1.23±0.03	1.26±0.02
0.15	1.67±0.01	1.70±0.02	1.80±0.04	1.78±0.03	1.60±0.01	1.63±0.01
0.20	2.23±0.02	2.19±0.02	2.36±0.03	2.32±0.03	2.05±0.01	2.11±0.01
0.25	2.65±0.01	2.70±0.02	2.72±0.11	2.85±0.02	2.46±0.03	2.53±0.02
0.30	3.03±0.02	3.10±0.02	3.14±0.22	3.24±0.02	2.79±0.02	2.91±0.01
0.35	3.38±0.01	3.44±0.01	3.56±0.03	3.58±0.01	3.12±0.01	3.24±0.01
0.40	3.65±0.01	3.75±0.01	3.82±0.02	3.88±0.01	3.37±0.02	3.54±0.01
0.45	3.86±0.01	3.98±0.01	4.02±0.01	4.12±0.01	3.59±0.01	3.80±0.01
0.50	4.06±0.01	4.18±0.02	4.23±0.03	4.30±0.02	3.79±0.02	4.00±0.02
0.55	4.21±0.02	4.34±0.02	4.32±0.02	4.48±0.02	3.94±0.02	4.21±0.02
0.60	4.32±0.02	4.46±0.02	4.44±0.02	4.61±0.02	4.05±0.02	4.34±0.03
0.65	4.43±0.02	4.60±0.02	4.54±0.02	4.76±0.02	4.14±0.02	4.52±0.03
0.70	4.59±0.02	4.75±0.03	4.69±0.02	4.94±0.01	4.30±0.02	4.64±0.02
0.75	4.77±0.03	4.99±0.02	4.86±0.02	5.14±0.06	4.44±0.03	4.85±0.02
0.80	4.90±0.03	5.13±0.03	4.97±0.03	5.27±0.06	4.54±0.02	5.01±0.04
0.85	4.97±0.02	5.20±0.03	5.08±0.03	5.36±0.05	4.65±0.02	5.16±0.04
0.90	5.01±0.02	5.26±0.03	5.09±0.02	5.41±0.02	4.73±0.02	5.21±0.03
0.95	5.05±0.02	5.26±0.03	5.11±0.01	5.35±0.02	4.74±0.02	5.25±0.02
1.00	5.05±0.03	5.27±0.02	5.11±0.04	5.38±0.03	4.77±0.02	5.24±0.02

at $T=270$ and 370 K is plotted in Fig. 2. The measured energies are in quite good agreement with previous measurements on alloys of similar composition.[9,10] The results are similar to those obtained in the Cu-Al-Be system. The energies exhibit anomalous temperature dependence and a slight saddle point is observed in the vicinity of $q=\frac{2}{3}$ (110).

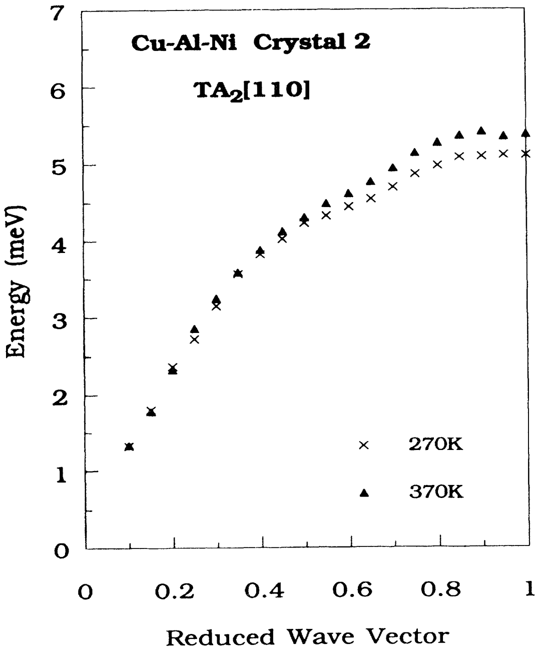

FIG. 2. $TA_2[100]$ phonon-dispersion curve of Cu-Al-Ni crystal 2 at $T=270$ and 370 K.

The Cu-Al-Be results were also compared with measurements performed under the same instrumental conditions on a Cu-Zn-Al alloy. The measured energies, summarized in Fig. 3 and tabulated in Table III, are in quite good agreement with previous measurements on an alloy of similar composition.[11,12] The results on this alloy also are similar to those obtained on the Cu-Al-Be and Cu-Al-Ni alloys.

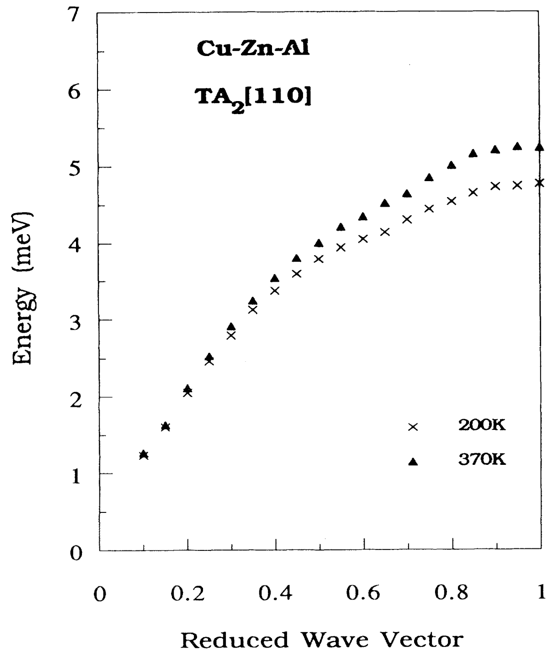

FIG. 3. $TA_2[110]$ phonon-dispersion curve of Cu-Zn-Al crystal at $T=200$ and 370 K.

In the experiments on the Cu-Al-Be system no evidence of any elastic peaks related to the martensite structure was found within the bcc temperature range of the system. We also did not find any elastic peaks in the two Cu-Al-Ni samples examined in this study, although such peaks were observed in a previous study of this system.[10] On the other hand, an elastic peak at $q \approx \frac{1}{3}$ (110) was found in transverse $[1\bar{1}0]$ scans in our study of the Cu-Zn-Al sample, as in a previous study[11] on a sample of similar composition. The intensity of this peak, originating from three distinct small parts of the crystal, increased as the temperature decreased towards the transition temperature. The intensity and temperature dependence of this peak at temperatures above the transition temperature was found to depend on the number of times the sample was cycled through the transition temperature and the time the sample was kept below the transition. Presumably these three embryos of the martensitic phase were formed by local strains developed as a result of the quenching or by cycling the sample through the transition temperature. It is interesting that the existence of such embryos was assumed in the modulated lattice-relaxation model of the premartensite state proposed by Yamada and collaborators.[13–16]

The similarity of the results obtained on these various Cu-based alloys with quite a range of transition temperatures and compositions strongly suggests that the behavior of the $TA_2[110]$ is characteristic of these alloys. In particular, the behavior of the $\frac{2}{3}$ (110) phonon involved in the transformation to the 18R (Cu-Al-Be) or 9R (Cu-Zn-Al) is not different from that of the zone-boundary phonon which is involved in the transformation to the 2H structure (Cu-Al-Ni). Therefore, it is not possible from the temperature dependence of the phonon energies of the $TA_2[110]$ branch of these alloys to predict the structure of the close-packed martensitic phase. A similar result was obtained in a recent study[17] of the lattice dynamics of bcc La. Although bcc La transforms to fcc, the $T_1[110]$ branch of this metal is similar to that of bcc Zr which transforms to the hcp structure.[17,18] This similarity is due to the fact that the bcc structure is inherently unstable towards the formation of close-packed structures involving displacements of the TA[110] phonon modes. If one or several of these structures are favored energetically, the dynamical distortion of the bcc phase toward the martensite structure(s), irrespective of the mode(s) involved, introduces strong anharmonic effects that affect the entire TA[110] branch.

In summary, the phonon modes of the $TA_2[110]$ branch of Cu-based-alloy crystals with transition temperatures ranging from approximately 160 to 240 K have very low energies and exhibit anomalous temperature dependence. A slight anomaly at $q = \frac{2}{3}$ was observed in the $T_2[110]$ branch of all these alloys; this anomaly seems to be a common characteristic of these Cu-based alloys and, therefore, cannot be considered as a precursor of the transition to the 18R structure.

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