Brief Reports

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High-pressure ultrasonic study of vibrational anharmonicity in bcc Cu-Al-Be alloys

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To quantify the vibrational anharmonicity of the long-wavelength acoustic modes of bcc $Cu_{74.1}Al_{23.1}Be_{2.8}$ near its martensitic transition temperature M_s (261 K), the hydrostatic pressure derivatives $(\partial C_{IJ}/\partial P)_{P=0}$ of the elastic stiffness moduli have been measured. The Grüneisen parameters at 268 K (just above M_s), especially of longitudinal modes, which become smaller than those of the shear modes, are quite different from those at 295 K: the anharmonicity changes markedly in the vicinity of the transition. Similar trends are noted for $Cu_{66.5}Al_{12.7}Zn_{20.8}$. Experimental data near M_s are used to estimate cubic invariants in the strain order parameters in a Landau formalism.

Many metals, including bcc Cu-based alloys, undergo a first-order martensitic transition from a high-temperature bcc phase to a close-packed structure on lowering the temperature. It has been established experimentally[1-3] that the bcc phase is stabilized by a large vibrational entropy due to a low-energy transverse phonon branch, as suggested by Zener.[4] Although such transitions are driven principally by a shear, the detailed microscopic nature of the mechanism remains a source of debate.[5] To understand the dynamics of displacive transitions, it is necessary to go beyond the harmonic approximation. For an elastic phase transition, the condensation at T_c involves freezing-in of the soft-mode displacement; as the corresponding elastic stiffness diminishes, soft-mode anharmonicity becomes increasingly important and eventually leads to the transition. An example is the weakly first-order fcc to fct displacive transition in In-Tl alloys; experimental determination of the higher-order invariants in the order parameter—a strain tensor component—has established quantitatively this role of anharmonicity.[6,7] However the martensitic transition undergone by bcc alloys is not elastic: The point group of the product phase is not a subgroup of the parent phase. Therefore, the mechanism is not simply a result of softening of the shear acoustic-phonon mode associated with the small $C'[=(C_{11}-C_{12})/2]$; only partial softening is needed.[3,8,9] For many bcc metals the transverse phonon modes in the Σ_4 branch along $\langle 110 \rangle$ directions have small energies; displacements associated with their eigenvectors, through anharmonic coupling to the elastic strain, can be involved in the transition mechanism and can be described phenomenologically by an anharmonic Landau free-energy expansion with a uniform strain together with a shuffle mode as order parameters.[9,10] Recently, a lattice-dynamical model has been proposed,[11] in which anharmonic interactions lower the phonon frequencies, conforming to this mechanism. Strain fluctuations caused by vibrational anharmonicity can drive these first-order transitions.[12]

The previous studies have emphasized the necessity of quantifying the vibrational anharmonicity of the β bcc phase near M_s. However experimental data on the higher-order terms in the strain Hamiltonian are sparse, although some measurements of the second (SOEC) and third-order elastic constants (TOEC) are available for Cu-Zn-Al alloys.[13] The main objective here is to provide quantitative information on the anharmonicity of long-wavelength acoustic modes in a bcc $Cu_{74.1}Al_{23.1}Be_{2.8}$ single crystal just above its transition temperature M_s (261 K Ref. 3) to the 18 R martensitic structure. The hydrostatic pressure derivatives $(\partial C_{IJ}/\partial P)_{P=0}$ of the elastic stiffnesses determined ultrasonically are used to obtain the Grüneisen parameters, defining the anharmonicity of the long-wavelength acoustic modes, which are compared with those computed from TOEC data[13] for $Cu_{66.5}Al_{12.7}Zn_{20.8}$.

To determine the effects of temperature and pressure on the ultrasonic wave transit time, a pulse-echo overlap system capable of measuring changes to 1 part in 10^5 in ultrasonic transit time was used. Hydrostatic pressures up to 0.15 GPa were applied using a piston and cylinder apparatus with silicone oil as the pressure transmitting medium. Pressure was measured using a precalibrated manganin resistance gauge. Pressure induced changes in the sample dimensions were taken into account by using the "natural velocity (W)" technique. For further details of the experimental setup see Ref. 14.

The adiabatic SOEC of $Cu_{74.1}Al_{23.1}Be_{2.8}$ measured at 295 and 268 K (Table I) and their temperature dependences agree with previous data.[3] The shear stiffness C' is very small and reduces markedly as the temperature is lowered towards M_s. For all modes the ultrasonic wave velocities increase linearly with pressure. The derivatives $(\partial C_{IJ}/\partial P)_{P=0}$ at 295 K (Table I) follow the usual trend

observed for bcc metals:[15]

$$(\partial C_{11}/\partial P)_{P=0} \sim (\partial C_{12}/\partial P)_{P=0} > (\partial C_{44}/\partial P)_{P=0} > (\partial C'/\partial P)_{P=0} .$$

For bcc In-Tl alloys $(\partial C_{IJ}/\partial P)_{P=0}$ measurements showed that the anharmonic contribution ΔG_{anh} to the Gibbs free energy is substantially less than the harmonic contribution $\Delta G_h (= T\Delta S_h = 0.35$ kT).[15] This is also true for $Cu_{74.1}Al_{23.1}Be_{2.8}$ confirming that the stability of the bcc form accrues largely from the harmonic contributions to the excess entropy from modes with propagation vector $\mathbf{N}\langle 110\rangle$ and polarization vector $\mathbf{U}\langle 1\bar{1}0\rangle$.[13]

The pressure derivative $(\partial C'/\partial P)_{P=0}$ of the soft shear mode modulus is rather larger at 268 K than that at 295 K (Table I). Although the temperature dependences of SOEC show that only C' softens as $Cu_{74.1}Al_{23.1}Be_{2.8}$ approaches M_s, there are pronounced decreases in the values of $(\partial C_{11}/\partial P)_{P=0}$, $(\partial C_L/\partial P)_{P=0}$, and $(\partial B^S/\partial P)_{P=0}$ as the temperature is reduced from 295 to 268 K, indicating that third-order terms in the strain free energy involving volume dependence are also affected as the material approaches the transition. $(\partial C_{44}/\partial P)_{P=0}$ is almost independent of temperature. The three TOEC combinations, obtainable from the C_{IJ} and $(\partial C_{IJ}/\partial P)_{P=0}$ data, also show a marked temperature dependence (Table I): The interaction responsible for the martensitic transition affects the cubic terms in addition to the harmonic term.

The pressure variations of SOEC are consequences of acoustic-mode anharmonicity. The long-wavelength acoustic-mode Grüneisen parameters $\gamma_p(\vec{N})$ of $Cu_{74.1}Al_{23.1}Be_{2.8}$ computed at 295 and 268 K are plotted as a function of mode propagation direction in Fig. 1(a). At room temperature, about 35 K above M_s, the $\gamma_p(\vec{N})$ show normal behavior having magnitudes in the usual range for bcc metals. The longitudinal mode $\gamma_p(\vec{N})$ are larger than those associated with shear modes. The $\gamma_p(\vec{N})$ in a given branch do not vary substantially with propagation direction. However, the $\gamma_p(\vec{N})$ determined at 268 K are quite different [Fig. 1(a)]. In particular, somewhat unexpectedly, the longitudinal mode gammas have decreased drastically (by about 40%) becoming smaller than those of the shear modes; longitudinal-mode anharmonicity has been reduced near the transition. In contrast the $\gamma_p(\vec{N})$ for the $\mathbf{N}\langle 110\rangle\mathbf{U}\langle 1\bar{1}0\rangle$ shear mode, associated with C', becomes substantially larger: The soft-mode anharmonicity increases near the transition. Softening takes place throughout conelike regions centered on the $\mathbf{N}\langle 110\rangle\mathbf{U}\langle 1\bar{1}0\rangle$ axes, behavior reflected in the $\gamma_p(\vec{N})$. The $\gamma_p(\vec{N})$ of the transverse mode branch, which along the $\langle 100\rangle$ directions can be associated with C_{44} (a two-dimensional manifold), remain essentially unaltered with temperature [Fig. 1(a)].

The small C' of $Cu_{74.1}Al_{23.1}Be_{2.8}$ conforms with the expectation that a bcc structure exhibits little resistance to

TABLE I. The elastic and nonlinear acoustic properties, and the vibrational anharmonicities of long-wavelength acoustic modes expressed in terms of TOEC combinations and the mean acoustic Grüneisen parameter $\bar{\gamma}^{el}$ (calculated using $\sum_{p=1}^{3}\int_\Omega \gamma_p(\vec{N})d\Omega / \int_\Omega 3d\Omega$) at 295 and 268 K for $Cu_{74.1}Al_{23.1}Be_{2.8}$ alloy single crystal.

	Temperature (K)	
	295	268
SOEC (GPa)		
C_{11}	134.2	134.4
C_{12}	119.9	120.3
C_{44}	96.5	97.6
C'	7.14	7.05
C_L	223.6	225.0
Bulk modulus B^s	124.7	125.0
Pressure derivatives of SOEC		
$(\partial C_{11}/\partial P)_{P=0}$	5.0	3.1
$(\partial C_{12}/\partial P)_{P=0}$	4.6	2.5
$(\partial C_{44}/\partial P)_{P=0}$	2.6	2.8
$(\partial C'/\partial P)_{P=0}$	0.19	0.31
$(\partial C_L/\partial P)_{P=0}$	7.4	5.6
$(\partial B^s/\partial P)_{P=0}$	4.7	2.7
TOEC combinations (GPa)		
$C_{111}+2C_{112}$	−2380	−1670
$C_{144}+2C_{166}$	−1440	−1520
$C_{123}+2C_{112}$	−1470	−680
$\bar{\gamma}^{el}$	1.69	1.61
Thermal Grüneisen parameter γ^{th}	1.5	

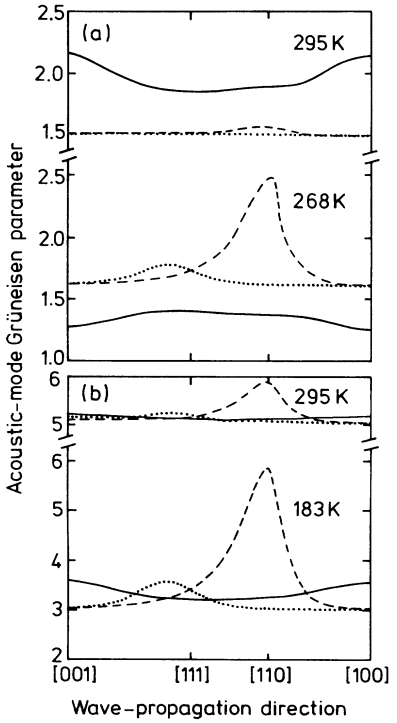

FIG. 1. Long-wavelength, longitudinal (solid line) and shear (dashed and dotted lines) acoustic-mode Grüneisen parameters of monocrystalline (a) $Cu_{74.1}Al_{23.1}Be_{2.8}$ (at 295 and 268 K) and (b) $Cu_{66.5}Al_{12.7}Zn_{20.8}$ (at 295 and 183 K) as a function of mode propagation direction.

a $\{110\}\langle 1\bar{1}0\rangle$ shear. Application of pressure results in a small increase of C': $(\partial C'/\partial P)_{P=0}$ is small but positive (Table I). Furthermore $(\partial C'/\partial P)_{P=0}$ becomes larger at 268 K near M_s, behavior reflected in an increase of the $\gamma_p(\vec{N})$ for the $\mathbf{N}\langle 110\rangle\mathbf{U}\langle 1\bar{1}0\rangle$ shear mode [Fig. 1(a)]. This aspect of $Cu_{74.1}Al_{23.1}Be_{2.8}$ is quite different in kind from that observed near the elastic transition in fcc In-Tl alloys, where softening of the C' mode is accompanied by a negative $(\partial C'/\partial P)_{P=0}$ and a large negative Grüneisen parameter.[6]

Do these observations concerning the anharmonicity extend to related Cu-based bcc alloys? They do. The $\gamma_p(\vec{N})$ computed at 295 and 183 K from the TOEC measured[13] for $Cu_{66.5}Al_{12.7}Zn_{20.8}$ are plotted in Fig. 1(b). Although the lowest temperature (183 K) at which the measurements were made is somewhat above M_s (158 K), the trends for $Cu_{66.5}Al_{12.7}Zn_{20.8}$ are similar to those found for $Cu_{74.1}Al_{23.1}Be_{2.8}$.

To describe the bcc to 9 R transformation Gooding and Krumhansl[10] employed a Ginzburg-Landau-Wilson effective free energy, which included the strains associated with the $\mathbf{N}\langle 110\rangle\mathbf{U}\langle 1\bar{1}0\rangle$ acoustic modes and also displacements

$$\Psi = A\hat{e}_{[1\bar{1}0]}\sin(\{\mathbf{q}\cdot\mathbf{r}\}+\theta) \tag{1}$$

of the $(\frac{1}{3},\frac{1}{3},0)$ Σ_4 phonon. A test of this approach requires an experimental evaluation of the free-energy density in a similar way to that carried out for the elastic transition in In-Tl alloys.[7] To obtain the strain terms, it is necessary to work with the symmetry adapted strain tensor combinations, which form bases for the irreducible representations. For a cubic crystal, the strain tensor components, which act as eigenvectors, can be written in terms of Lagrangian strains η_{ij} as[6,16,17]

$$\begin{aligned}
&\eta_0^0=\eta_{11}+\eta_{22}+\eta_{33}\ ;\ A\ ,\\
&\eta_1=(2\eta_{33}-\eta_{22}-\eta_{11})/\sqrt{3}\ ,\ \eta_1'=(2\eta_{11}-\eta_{33}-\eta_{22})/\sqrt{3}\ ,\ \eta_1''=(2\eta_{22}-\eta_{11}-\eta_{33})/\sqrt{3}\ ;\ E\ ,\\
&\eta_2=\eta_{11}-\eta_{22}\ ,\ \eta_2'=\eta_{22}-\eta_{33}\ ,\ \eta_2''=\eta_{33}-\eta_{11}\ ;\ E\ ,\\
&\eta_3=\eta_{23}\ ,\ \eta_4=\eta_{13}\ ,\ \eta_5=\eta_{12}\ ;\ T\ .
\end{aligned} \tag{2}$$

Transformation of the elastic free energy from finite Lagrangian strain tensor space to the irreducible strain space leads to[6,17]

$$\begin{aligned}
\phi=&\tfrac{1}{6}(C_{11}+2C_{12})(\eta_0^0)^2+\tfrac{1}{4}(C_{11}-C_{12})(\eta_1^2+\eta_2^2)+\tfrac{1}{2}C_{44}(\eta_3^2+\eta_4^2+\eta_5^2)\\
&+\tfrac{1}{54}(C_{111}+6C_{112}+2C_{123})(\eta_0^0)^3+\tfrac{1}{12}(C_{111}-C_{123})\eta_0^0(\eta_1^2+\eta_2^2)\\
&+\frac{1}{24\sqrt{3}}(C_{111}-3C_{112}+2C_{123})\eta_1(\eta_1^2-3\eta_2^2)+\tfrac{1}{6}(C_{144}+2C_{155})\eta_0^0(\eta_3^2+\eta_4^2+\eta_5^2)\\
&+\frac{1}{4\sqrt{3}}(C_{144}-C_{155})\eta_1(2\eta_5^2-\eta_4^2-\eta_3^2)+\tfrac{1}{4}(C_{144}-C_{155})\eta_2(\eta_3^2-\eta_4^2)+C_{456}\eta_3\eta_4\eta_5\\
&+\tfrac{1}{192}(C_{1111}-2(C_{1112}+C_{1113})+3C_{1123})(\eta_1^2+\eta_2^2)^2\ .
\end{aligned} \tag{3}$$

A linear combination of the three order parameters η_1, η_2, and Ψ represents the symmetry-breaking displacement that develops the 9 or 18 R structure from the bcc structure; the required free-energy density, superseding that given in Ref. 10, is

$$\begin{aligned}
\Phi=&\phi+\tfrac{1}{2}r_0|\Psi|^2+\tfrac{1}{4}u_0|\Psi|^4+\tfrac{1}{6}v_0|\Psi|^6+\tfrac{1}{6}v_1[\Psi^6+(\Psi^*)^6]\\
&+\tfrac{1}{8}w_0|\Psi|^8+z_0[\Psi^3+(\Psi^*)^3]\ .
\end{aligned} \tag{4}$$

The large effects near M_s on the longitudinal mode $\gamma_p(\vec{\mathbf{N}})$, and the first-order character of the transition involving a large entropy change ΔS, show that a significant volume change is also incurred. So, as previously suggested,[9] symmetry nonbreaking terms ϕ_{snb}, involving the identical irreducible representation η_0^0,

$$\begin{aligned}
\phi_{\text{snb}}=&\tfrac{1}{6}(C_{11}+2C_{12})(\eta_0^0)^2\\
&+\tfrac{1}{54}(C_{111}+6C_{112}+2C_{123})(\eta_0^0)^3\\
&+\tfrac{1}{648}(C_{1111}+8C_{1112}+6C_{1122}+12C_{1123})(\eta_0^0)^4
\end{aligned} \tag{5}$$

must also be included in the free-energy Eq. (4). Cross terms in η_0^0, η_1, and η_2 with forms given in Ref. 17 could also be large enough to be involved.

Some progress can now be made towards evaluation of the contributions to the free energy from the strain tensor components for $Cu_{74.1}Al_{23.1}Be_{2.8}$ and $Cu_{66.5}Al_{12.7}Zn_{20.8}$. The cubic invariants for $(\eta_0^0)^3$ in the symmetry nonbreaking part of the elastic strain energy are given by

$$B(\partial B/\partial P)_{P=0}=(C_{111}+6C_{112}+2C_{123})/9\ . \tag{6}$$

For $Cu_{74.1}Al_{23.1}Be_{2.8}$ this quantity is 586 GPa at 295 K and it has reduced to 337 GPa at 268 K; for $Cu_{66.5}Al_{12.7}Zn_{20.8}$ (from the TOEC data[13]) it is 1142 GPa at 293 K and 771 GPa at 183 K. These large changes in the invariant of $(\eta_0^0)^3$, incurred as the temperature is reduced towards M_s, confirm the necessity of including the effect of volume in the strain free energy when considering this first-order transition. Nevertheless the more im-

portant terms in the free-energy calculation are those in η_1 and η_2. The corresponding TOEC combination associated with the vibrational anharmonicity is $(C_{111}-3C_{112}+2C_{123})$ [see Eq. (3)], which is -7.4 GPa at 293 K and -8.2 GPa at 183 K for $Cu_{66.5}Al_{12.7}Zn_{20.8}$. Work is now in hand to determine the TOEC of $Cu_{74.1}Al_{23.1}Be_{2.8}$ to provide further numerical values of the anharmonic terms in the strain free energy associated with the bcc to 18 R martensitic transition.

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