

Martensitic transformation of Cu-based shape-memory alloys: Elastic anisotropy and entropy change

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We have studied the martensitic transformation in a family of Cu-Al-Be crystals: We have measured the entropy change of the transition using a high-sensitivity calorimeter, and the elastic anisotropy of the high-temperature phase as a function of temperature by an ultrasonic method. Both entropy change and elastic anisotropy at the transition temperature are shown to be independent of the alloy composition. On the other hand, the vibrational entropy change and the elastic anisotropy have been theoretically related by an expression containing the fraction of low-energy modes. This relation has been specified for two different situations: (i) The region of soft modes is limited to wave vectors very close to the $[\xi\xi0]$ direction in the reciprocal space and (ii) the region of soft modes is allowed to spread up to wave vectors with directions differing substantially from $[\xi\xi0]$. Our experimental results and other results for other families of Cu-based alloys are consistent with the two relations, suggesting a small (or at least composition independent) electronic contribution to the total entropy change.

I. INTRODUCTION

Martensitic transformations (MT's) are first-order diffusionless solid-solid phase transitions, taking place from a bcc high-temperature phase (H) to a close-packed low-temperature phase (L), where the resultant lattice distortion can be essentially described by a shear.^{1,2} Typical examples can be found in alkali metals (Li, Na, etc.),³ transition metals (Ti, Zn, Hf, etc.),⁴ and a number of alloys (many noble metal-based alloys, Ni-Al, Ni-Ti, etc.).⁵ In Cu-based alloys, this kind of transition has been subject of extensive research because of the technologically important shape-memory properties exhibited by these materials.⁶ In recent years most interest has been devoted to a number of peculiar features of the transition, including premonitory effects where anomalies in the elastic constants and phonon-dispersion curves are observed.⁷ Phonon-dispersion curves show a low-energy TA branch with dip at a certain wave number q_0 ($\neq 0$), characteristic of the L structure, and also a low value of a shear elastic constant. Both the energy of these low-energy phonons and the shear elastic constant decrease on approaching the transition during cooling, but neither of these two magnitudes attains a zero value at the transition temperature (M_s), as would be the case in a typical second-order soft-mode phase transition.⁸

The importance of the large vibrational entropy of the H phase in deriving this kind of transition has been recognized after the work of Friedel.⁹ The situation can be summarized as follows: The close-packed structure is energetically more favorable, but the bcc (open structure) H phase is stabilized by its large phonon (vibrational) entropy. Upon cooling, a transition occurs from the soft parent phase to a stiffer martensitic phase. In his work, Friedel imputed this behavior mainly to the fact that the coordination number of the bcc phase is smaller than the

coordination number of the close-packed structure. Recent inelastic neutron-diffraction experiments, carried out by Heiming, Petry, and Trapenau,¹⁰ have shown that the bcc phase in pure metals of the groups 3 and 4 is stabilized by short-wavelength modes rather than by long-wavelength modes, as first suggested in the pioneering work of Zener.¹¹

The present paper is devoted to investigating experimentally the possibility of a relationship between the entropy decrease achieved in the transition and the elastic properties of the bcc phase near the MT. For this purpose we have studied a family of composition-related Cu-Al-Be alloys transforming from a β bcc phase to a 18R martensitic structure. It is known that very small changes in composition lead to drastic modifications in transformation temperatures,¹² for these particular alloys, a change in 1% Be modifies M_s by as much as 100 K.¹³ We have investigated alloys transforming at temperatures ranging from room temperature down to 100 K. The entropy change of the transition has been measured using high-sensitivity calorimetry, and the elastic constants of the parent phase have been obtained by ultrasonic methods. Our results have been compared with results for other Cu-based alloys transforming to the 18R and 2H martensitic structures.

II. EXPERIMENT

A collection of Cu-Al-Be single crystals with variable Be content and a polycrystal of intermediate composition have been investigated; their atomic composition is given in Table I. From the original rods, samples for both calorimetric and elastic-constant measurements were cut using a low-speed diamond saw. Calorimetric samples were typically around 14 mm in diameter and 1–2 mm thickness. Samples for elastic-constant measurements,

TABLE I. Atomic composition of the different alloys investigated.

Alloy	Cu	Al	Be
A	74.08	23.13	2.79
B	74.24	22.84	2.91
C	73.98	23.06	2.97
D ^a	73.52	23.28	3.19
E	73.73	22.72	3.55
F	73.12	22.31	4.58

^aPolycrystal.

about 10 mm in length, were cut from the monocrystalline specimens with two planes parallel to the (110) planes of the parent phase, with an accuracy better than 2°. The samples were polished flat to surface irregularities of about 2 μm and parallel to better than 10^{-3} rad.

A. Calorimetric measurements

Differential-scanning-calorimetry measurements have been conducted for all the crystals to measure the transformation temperatures and thermal powers released or absorbed during the forward and reverse thermally induced martensitic transformations. The instrument used, a high-sensitivity microcalorimeter (about 400 mV W⁻¹ at room temperature),¹⁴ employs two semiconducting thermoelectric power elements as heat-flow transducers, mounted differentially on top of a massive copper block of large thermal inertia. The temperature of the copper block is monitored by the Pt-100 probe of a platinum resistance thermometer. This temperature and the output differential voltage from the heat-flow transducers are collected by a computer-based data-acquisition system at typical rates of around 0.5 Hz. In this series of experiments, specimens have been scanned over temperatures in the range 100–300 K at rates around 1 K min⁻¹.

Heats exchanged during both forward and reverse transformations can be obtained by integration of the recorded thermal curves. A proper choice of the integral limits has come out to be particularly difficult in the present experiments, because all the thermograms happened to display very long tails in the low-temperature side of the transformation (the martensitic region), result-

ing in transformation temperature ranges as large as 60 K. This appears to be a characteristic feature of the thermally induced transition in Cu-Al-Be alloys. For this reason a base line extending between two preselected temperatures (well above and below the transformation range) and proportional to the fractional energy below the calorimetric peak at each temperature has been constructed using an iterative integral method.¹⁵ This has enabled automated calculation of $Q^{H \rightarrow L}$ and $Q^{L \rightarrow H}$ with uncertainties around 5%. Results for the five alloys studied are presented in Table II, together with their transformation temperatures (M_s and M_f for the forward transition, A_s and A_f for the reverse one). The values presented are averages over two to three different cycles. A collection of experimental thermal curves is shown in Fig. 1.

In principle, the latent heat of transformation does not equate the heat measured in the calorimeter because of additional contributions arising from the storage of elastic strain and interfacial energies and from irreversible energy losses.¹⁶ This is the reason why the absolute value $|Q^{H \rightarrow L}|$ is systematically lower than $|Q^{L \rightarrow H}|$. On the contrary, the integral of dQ/T over the transformation does not show systematic differences between forward and reverse directions. This fact, under the assumption of no difference in heat capacity between the two phases at the transition, evidences a negligibly small entropy production and enables computing the entropy change of transformation, ΔS , as an average of these two integrals. In this framework the latent heat of transformation is then given by $T_0 \Delta S$, where T_0 is the equilibrium transformation temperature. For this kind of transition, T_0 can be evaluated as $(M_s + A_f)/2$.¹⁶

Values for latent heats and entropy changes are presented in Table II. The constancy of ΔS for the alloys investigated shows up as a remarkable feature. This in contrast to the latent heat of transformation, whose composition dependence parallels that of M_s .

B. Measurement of elastic constants and their temperature dependence

Elastic constants have been determined using a pulse-echo ultrasonic method. Both X- and Y-cut quartz transducers have been used to generate and detect 10-MHz ultrasonic pulses. Acoustic coupling between sample and

TABLE II. Martensitic start (M_s) and finish (M_f) temperatures, reverse start (A_s) and finish (A_f) temperatures, equilibrium temperature $T_0 = (M_s + A_f)/2$, heats exchanged during forward ($Q^{H \rightarrow L}$) and reverse ($Q^{L \rightarrow H}$) transformations, entropy change ΔS , and latent heat $T_0 |\Delta S|$ for Cu-Al-Be alloys. Estimated experimental uncertainties are ± 1 K for the transformation temperatures, less than 5% for the heats exchanged and around 5% for the entropy change.

Alloy	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_0 (K)	$Q^{H \rightarrow L}$ (J mol ⁻¹)	$Q^{L \rightarrow H}$ (J mol ⁻¹)	$ \Delta S $ (J mol ⁻¹ K ⁻¹)	$T_0 \Delta S $ (J mol ⁻¹)
A	261	230	247	271	266	-354	359	1.38	367
B	227	188	213	236	231	-297	297	1.37	316
C	228	189	212	238	233	-294	326	1.39	324
D	206	181	195	219	212	-259	288	1.36	288
E	145	115	124	152	148	-198	206	1.42	210

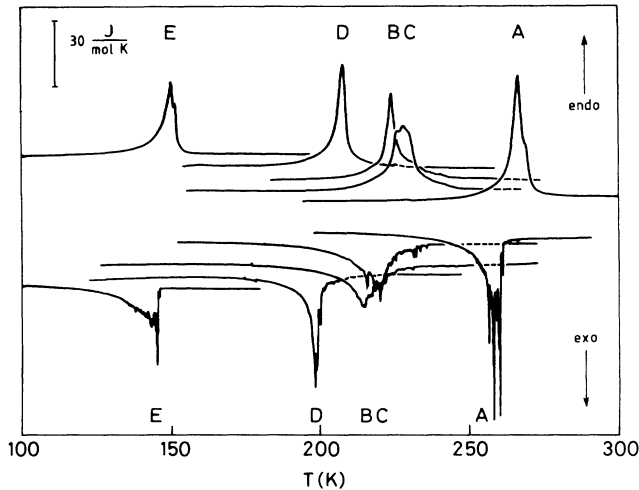


FIG. 1. Typical thermal curves for the alloys investigated, corresponding to the martensitic forward and reverse transformations.

transducer is optimized using Dow Resin 276-V9 and Nonaq Stopcock grease in the temperature ranges 210–350 and 77–to 270 K, respectively. The sample is placed on a copper plate whose temperature is monitored by an embedded Pt-100 probe of a platinum resistance thermometer. Typical heating and cooling rates center around 0.5 K min^{-1} . This is slow enough to ensure that the sample and copper plate are at the same temperature; nonetheless, a number of measurements have been carried out at other heating and cooling rates and at a constant temperature, and have confirmed that ultrasonic time measurements do not depend upon the heating and cooling rates.

Ultrasonic pulse transit times have been obtained using the phase-sensitive detection technique¹⁷ (MATEC, MBS-8000). An advantage of this technique over conventional pulse-echo overlap methods is the possibility of automated, computer-controlled measurements, allowing for a much larger amount of data to be acquired in a complete heating and cooling run. In our experimental setup, the temperature and change in ultrasonic transit

time are sequentially measured and transferred into a PC-compatible computer via IEEE 488. For heating and cooling rates around 0.5 K min^{-1} , a data pair is taken every 0.3 K approximately.

The velocity of ultrasonic waves has been measured along the [110] direction of the cubic parent phase. The adiabatic second-order elastic constants at room temperature of the four Cu-Al-Be single crystals considered for ultrasonic studies are shown in Table III. The values correspond to an average over three independent runs, and the error is the maximum deviation from the mean value. It is instructive to compare our results with the elastic constants of Cu-Al, quoted from literature,¹⁸ even if data for this alloy correspond to a different structural phase (fcc α at room temperature). C_L [$= (C_{11} + C_{12} + 2C_{44})/2$] and C_{44} coincide for all the Cu-Al-Be alloys, within the experimental uncertainties, and both values are slightly larger than the corresponding ones for Cu-Al. In contrast, the values of the elastic constant $C' [= (C_{11} - C_{12})/2]$ are different for the four alloys investigated and markedly different from the value corresponding to the close-packed Cu-Al system; Cu-Al-Be is much softer for a shear involving next-nearest neighbors, i.e., in the {110} planes along the [110] direction, as expected for an open bcc structure. The small values of C' result in high values for the elastic anisotropy ratio ($A = C_{44}/C'$), a feature intimately related to the fact that Cu-Al-Be alloys undergo a martensitic transition. Indeed, as shown in Table III, a smaller C' at room temperature corresponds to alloys closer to the martensitic transition temperature. Figures 2(a) and 2(b) display, as a function of the Be content, the transition temperature M_s , elastic constant C' , and elastic anisotropy A at both M_s and room temperature: M_s decreases linearly with Be content, in accord with previous measurements;¹³ it is also apparent that at room temperature C' increases with Be content, and since C_{44} is almost constant, the anisotropy decreases.

The temperature dependence of the elastic constants has been measured for different samples from about room temperature down to M_s . Below M_s the surface relief associated with the appearance of the martensitic domains breaks the acoustic couplings between the sample and transducer, and the ultrasonic echoes disappear. An ex-

TABLE III. Transition temperature M_s , elastic constants C_{IJ} at room temperature, relative thermal variation $\Gamma_{IJ} = C_{IJ}^{-1} dC_{IJ}/dT$, elastic anisotropy A at room temperature, elastic constants $C_{IJ}(M_s)$, and elastic anisotropy $A(M_s)$ at the transition temperature.

Alloy	M_s (K)	C_L (GPa)	C_{44} (GPa)	C' (GPa)	Γ_L (10^{-4} K^{-1})	Γ_{44} (10^{-4} K^{-1})	Γ' (10^{-4} K^{-1})	A	$C_{44}(M_s)$ (GPa)	$C'(M_s)$ (GPa)	$A(M_s)$
A	261	224.5 (± 0.4)	94.9 (± 0.6)	7.15 (± 0.04)	-2.33 (± 0.11)	-3.90 (± 0.01)	4.59 (± 0.10)	13.27	96.1	7.04	13.65
B	227	223.9 (± 0.6)	92.9 (± 1.2)	7.22 (± 0.1)	-2.35 (± 0.07)	-3.84 (± 0.02)	4.49 (± 0.27)	12.87	95.3	7.00	13.62
E	145	224.1 (± 0.3)	91.1 (± 0.2)	7.64 (± 0.04)	-2.19 (± 0.15)	-3.48 (± 0.24)	4.75 (± 0.59)	11.83	95.8	7.10	13.50
F		222.9 (± 6.0)	94.4 (± 1)	8.97 (± 0.30)	-2.11 (± 0.07)	-3.58 (± 0.11)	4.01 (± 0.09)	10.52			
Cu ₇₅ Al ₂₅ ^a		216.5	81.5	17.0	-2.2	-3.0	-4.8	4.8			

^aValues obtained by interpolation from data quoted in Ref. 18.

ample of evolution of the elastic constants with reduced temperature $T - M_s$ is shown in Fig. 3. It is worth pointing out that plotted data correspond to both heating and cooling runs which, as shown in the figure, superimpose perfectly. C_L and C_{44} behave as predicted by the standard anharmonic theory for solids: They increase linearly as temperature is reduced. A linear least-squares fit to the data gives the values for the relative change of elastic constants with temperature presented in Table III. Again, average values over three different experiments are listed together with their maximum deviation.

It is worth emphasizing that the shear modulus C' of all the alloys decreases upon reducing temperature, indicating a softening of the shear modes associated with C' . Similar behavior has already been reported for other noble-based alloys undergoing martensitic transformations.¹⁹ The decrease in C' with reducing temperature has been found to be linear; the corresponding slopes are also listed in Table III. No change in slope has been noted on approaching M_s , contrary to observations reported for Cu-Al-Ni by Hausch and Török.²⁰ Indeed, changes in slope are expected to occur when the sample transforms to the martensitic phase without a complete disappearance of the ultrasonic echoes. This behavior is

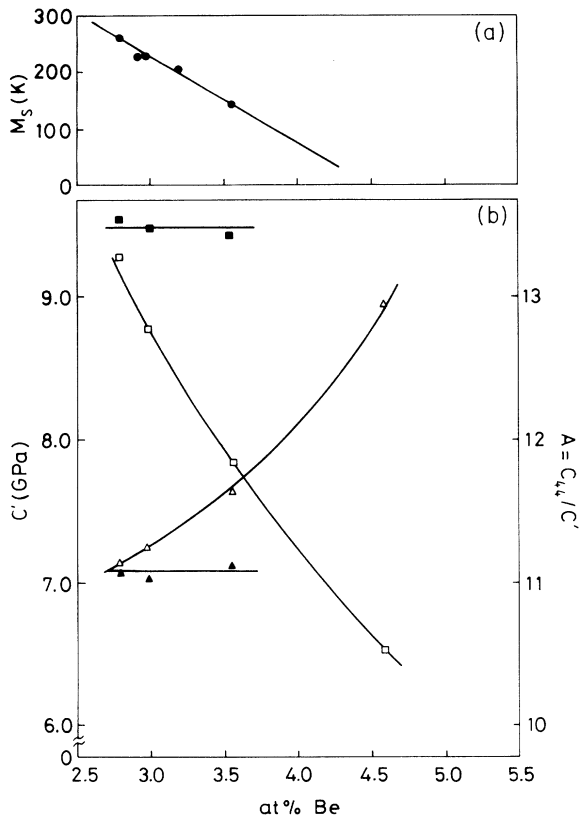


FIG. 2. (a) Martensitic transition temperature (M_s) as a function of berillium content. (b) Shear elastic constant C' (Δ , \blacktriangle) and elastic anisotropy A (\square , \blacksquare) as a function of berillium content. Open symbols represent values at room temperature; solid symbols represent values at the transition temperature M_s . The lines serve as guides to the eye.

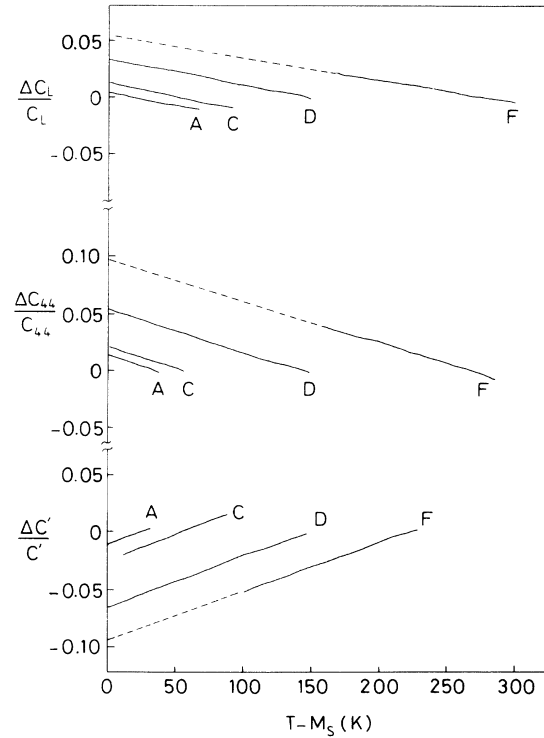


FIG. 3. Typical examples for the relative change of the elastic constants with the reduced temperature $T - M_s$.

exemplified in Fig. 4. The elastic constant shows a typical hysteretic behavior, related to the fact that the sample has transformed (partially) into martensite. The decrease in C' found in our measurements is a manifestation of the tendency of the bcc structure to become mechanically unstable.

The composition dependence of the slopes dC'/dT and dC_{44}/dT has been considered. These quantities can be computed from the values in Table III: Both seem to increase slightly with Be content. The observed increase, however, is very small and falls within the limits of experimental uncertainties.

The values of $C_{44}(M_s)$, $C'(M_s)$, and $A(M_s)$ at the transition temperature are also listed in Table III, and $C'(M_s)$ and $A(M_s)$ are plotted in Fig. 2(b) as a function of Be content. An interesting result is that these two

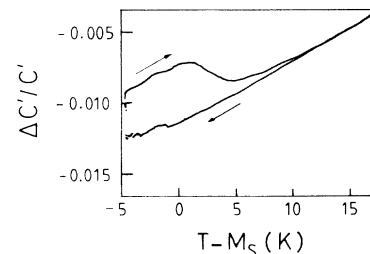


FIG. 4. Detailed view of the relative change of C' as a function of the reduced temperature ($T - M_s$) for alloy D, which has partially transformed to martensite, showing hysteresis.

quantities are remarkably coincident for all the alloys investigated. Moreover, the transformation temperature for alloy F can be extrapolated from the dependence of M_s on composition [Fig. 2(a)], resulting in $M_s \sim -10$ K; actually, we have checked that this alloy does not transform down to liquid-helium temperature. Then extrapolation of C_{44} and C' for alloy F at its expected M_s renders a value of the elastic anisotropy of around 13.3, in very good agreement with values for the rest of the alloys. Therefore, present experiments clearly demonstrate that the elastic anisotropy in Cu-Al-Be alloys has a fixed value at the martensitic transition temperature. The behavior in the elastic anisotropy is mainly governed by the behavior of the elastic constant C' ; the role of C_{44} is practically irrelevant.

III. DISCUSSION

It is customary to consider that the entropy change at the MT stems from two main contributions:

$$\Delta S_{\text{tot}} = \Delta S_{\text{vib}} + \Delta S_{\text{elec}}, \quad (1)$$

where ΔS_{vib} is the vibrational contribution and ΔS_{elec} is the contribution of the electrons near the Fermi surface. Configurational contributions are absent in the case of a MT because of its diffusionless character. Heiming *et al.*,²¹ by means of inelastic neutron-diffraction experiments, have been able to evaluate the relative importance of these two contributions in the MT of Zr and have obtained that ΔS_{vib} is the dominant term, contributing by about 65% to ΔS_{tot} .

Since ΔS_{vib} appears to be the relevant contribution in driving the MT, in the following we concentrate mainly on its analysis. Recently, Morris and Gooding²² have proposed a one-dimensional (1d) model to analyze the special features of this kind of first-order entropy-driven phase transition. An interesting conclusion of their work is that the system behaves essentially harmonically, except in a very small temperature region near the transition where anharmonic effects play a relevant role in driving the transition. According to this finding, the entropy change associated with the transition can be obtained from extrapolation of the harmonic behavior of both H and L phases. Keeping this result in mind, we will evaluate the vibrational entropy change at the MT within harmonic (or quasi-harmonic) theory. For this purpose following the work of Abbé, Caudron, and Pynn,²³ we assume that the phonon spectrum of the H -temperature phase may be approximated by the superposition of a Debye law and an Einstein peak, accounting for the fraction α of $\{110\}\{1\bar{1}0\}$ transverse modes (soft modes) of the system. Although this is somewhat a crude approximation to the reality, the phonon spectrum of Zr (Ref. 21) and Ti (Ref. 24), measured by Petry *et al.*, shows features in qualitative agreement with this assumption.

At low temperature, as first proposed by Friedel,⁹ we will consider that the characteristic frequency of the soft modes changes as a consequence of (i) the symmetry change (which implies a change of coordination numbers)

and (ii) a change in the strength of the bonds between atoms. Therefore, at high enough temperatures, this simple model give

$$\Delta S_{\text{vib}} = 3Nk_B \alpha \ln \left(\frac{\omega_H}{\omega_L} \right), \quad (2)$$

where we have assumed that the Debye temperature of the modes that do not soften is the same in both parent and martensitic phases.

Now the problem is to evaluate the characteristic frequencies of the H and L phases, ω_H and ω_L . If C_1 and C_2 represent the bond strength between nearest- and next-nearest-neighbor pairs, then, in the central force approximation;

$$\omega_H \sim \sqrt{C_2}, \quad \omega_L \sim \sqrt{C_1}, \quad (3)$$

where it is assumed that the bond strengths are equal in both H and L phases. Then it is readily obtained that

$$\Delta S_{\text{vib}} = \frac{3}{2} Nk_B \alpha \ln(m A^{-1}), \quad (4)$$

where m is a factor depending on the symmetry of both the H and L phases and A is the elastic anisotropy ($A = C'/C_{44}$). Assuming, for the sake of simplicity, that the L phase has a fcc structure (it can be obtained from the bcc H phase through a Bain mechanism), simple calculations lead to $m = \frac{3}{2}$, and therefore

$$\Delta S_{\text{vib}} = \frac{3}{2} Nk_B \alpha \ln\left(\frac{3}{2} A^{-1}\right). \quad (5)$$

Provided that α is independent of the alloy composition, the above expression leads to the conclusion that ΔS_{vib} will only depend on the value of A at the transition point.

Experimental results presented in the previous section showed that ΔS_{tot} and A have always the same value, irrespective of the temperature at which the system undergoes the MT. This finding is consistent with Eq. (5) above, provided that the electronic contribution to the whole entropy change does not show significant composition dependence in the narrow composition range investigated in this work.

The fraction α of transversal soft modes is difficult to evaluate. Romero and Ahlers,²⁵ considering all those states whose wave vector does not differ by more than 10° from the $[\xi\xi 0]$ direction in reciprocal space and taking into consideration that there are 12 equivalent $[\xi\xi 0]$ directions and three polarization branches, estimated a theoretical value of $\alpha \sim 0.03$. For Cu-Al-Be alloys, we can input the values of ΔS and A measured in this work into Eq. (5); this leads to a value $\alpha = 0.05$, in rather good agreement with the expected value proposed by Romero and Ahlers.

Two different experimental approaches have been undertaken in order to evaluate α in Cu-Zn-Al alloys undergoing a MT from a bcc to a 18R structure. On the one hand, Abbé, Caudron, and Pynn²³ performed low-temperature C_p measurements which rendered a value $\alpha \sim 0.25$. On the other hand, Romero and Ahlers²⁵ measured the stress necessary to induce the transition at

liquid nitrogen and deduced $\alpha \sim 0.03$. A value of α as large as 0.25 would indicate that low-energy modes extend to states with wave vectors covering a rather broad range around the $[\xi\xi 0]$ direction. This being true, our Eq. (5) for the entropy change would no longer hold, since modes with polarizations different from $[110]$ must then be included when computing the characteristic frequencies appearing in Eq. (2). A simple expression for them would be²⁶

$$\frac{\omega_H}{\omega_L} \approx \left(\frac{q_1^H C_1 + q_2^H C_2}{q_1^L C_1} \right)^{1/2}, \quad (6)$$

which leads to

$$\Delta S = \frac{3}{2} N k_B \alpha \ln \left[\frac{q_1^H}{q_1^L} \right] \left[1 + \frac{q_2^H}{q_1^H} A^{-1} \right], \quad (7)$$

where $q_2^H = 6$, $q_1^H = 8$, and $q_1^L = 12$ are, respectively, the coordination numbers for nearest and next-nearest neighbors in the bcc phase and for nearest neighbors in the fcc phase. Again, this expression is consistent with our experimental results in Cu-Al-Be. Substitution of actual ΔS and A values for this alloy system gives $\alpha = 0.3$.

It seems difficult, at this point, to decide which of the two models better describes real systems. We suggest that inelastic neutron experiments in this kind of alloy would provide a definitive answer to this problem.

It is now interesting to compare the entropy change and elastic anisotropy of Cu-Al-Be obtained in the present investigation with results for other Cu-based alloys with similar characteristics. In Fig. 5 we have plotted the absolute value $|Q^{H \rightarrow L}|$ as a function of M_s for different Cu-Zn-Al and Cu-Al-Ni alloys. Our data for Cu-Al-Be are also included in the figure. For all these alloys, the ratio $|Q^{H \rightarrow L}|/M_s$ is a good approximation to the total entropy change.¹⁶ The Cu-Zn-Al alloys considered here transform from a bcc H phase to a $18R$

phase, while the Cu-Al-Ni alloys transform to a $2H$ close-packed structure. It appears from the figure that, for each family of alloys, $|Q^{H \rightarrow L}|$ is proportional to M_s , indicating a constant value for ΔS , independent of the composition, in each family. Moreover, it is apparent that $|Q^{H \rightarrow L}|$ for both Cu-Al-Be and Cu-Zn-Al alloys lies on a single straight line, different from the straight line for Cu-Al-Ni. This is evidence that the entropy change for both Cu-Al-Be and Cu-Zn-Al alloys is the same. We believe that this peculiarity is due to the fact that both alloys undergo a transition between the same H and L structures.

We have also quoted available values of the elastic anisotropy at the transition temperature for a family of composition-related Cu-Zn-Al alloys and for a Cu-Al-Ni

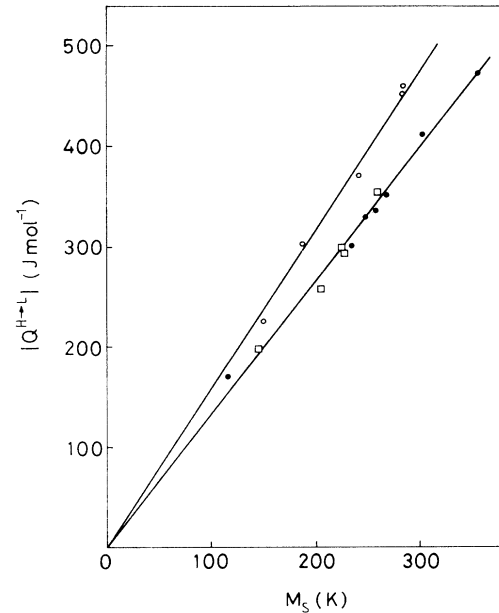


FIG. 5. Exchanged heat $|Q^{H \rightarrow L}|$ as a function of the transition temperature M_s . Data have been extracted from the following references, listed in order of increasing M_s : Cu-Zn-Al (●); 1. A. Planes, R. Romero, and M. Ahlers, *Scr. Metall.* **23**, 989 (1989); 2. J. Ortín and A. Planes, *Acta Metall.* **36**, 1873 (1988); 3. A. Planes, J. L. Macqueron, and J. Ortín, *Philos. Mag. Lett.* **57**, 291 (1988); 4. A. Planes, J. L. Macqueron, R. Rapacioli, and G. Guénin, *Philos. Mag. A* **61**, 221 (1990); 5. J. Viñals, V. Torra, A. Planes, and J. L. Macqueron, *ibid.* **50**, 653 (1984); 6. J. L. Macqueron (unpublished results); 7. M. Mantel, G. Guénin, J. L. Macqueron, J. Muntasell, R. Rapacioli, and A. Planes, *Scr. Metall.* **20**, 803 (1986). Cu-Al-Ni (○); 1, 2, 3, 5. C. M. Friend, J. Ortín, A. Planes, L. Mañosa, and M. Yoshikawa, *Scr. Metall. Mater.* **28**, 1641 (1990); 4. R. J. Salzbrenner and M. Cohen, *Acta Metall.* **27**, 739 (1979). Cu-Al-Be (□), present work. For all these alloys, Q/M_s is a good approximation to $\Delta S = \int dQ/T$. Note that Cu-Zn-Al and Cu-Al-Be data can be fitted to a straight line passing through the origin, and the same applies for Cu-Al-Ni data. The slope of these lines is approximately ΔS . Lines plotted in the figure give $\Delta S = 1.30 \text{ J K}^{-1} \text{ mol}^{-1}$ for Cu-Zn-Al and Cu-Al-Be alloys and $\Delta S = 1.59 \text{ J K}^{-1} \text{ mol}^{-1}$ for Cu-Al-Ni.

TABLE IV. Transition temperature M_s , elastic anisotropy at room temperature A , and elastic anisotropy at the transition temperature $A(M_s)$ for different Cu-based alloys.

Alloy ^a	M_s (K)	A	$A(M_s)$	Reference
Cu _{0.68} Zn _{0.16} Al _{0.16}	231	12.9	13.56	b
Cu _{0.66} Zn _{0.20} Al _{0.14}	177	12.4	13.57	b
Cu _{0.66} Zn _{0.21} Al _{0.13}	158	11.9	13.34	c
Cu _{0.63} Zn _{0.26} Al _{0.11}	21 ^d	10.9	13.25	b
Cu _{0.686} Al _{0.276} Ni _{0.037}	249	10.3	10.8	e

^aFor all Cu-Zn-Al alloys, the extrapolated value at M_s is obtained using $dC'/dT = 2.46 \times 10^6 \text{ Pa K}^{-1}$ and $dC_{44}/dT = -3.6 \times 10^7 \text{ Pa K}^{-1}$ [from Guénin *et al.* (Ref. 19)].

^bT. Suzuki, Y. Fujii, R. Kojima, and A. Nagasawa, in *Proceedings of ICOMAT'86* (The Japan Institute of Metals, Nara, 1986), p. 849.

^cB. Verlinden, T. Suzuki, L. Delaey, and G. Guénin, *Scr. Metall.* **18**, 975 (1984).

^dValue obtained from the dependence of M_s on composition [A. Planes, R. Romero, and M. Ahlers, *Acta Metall.* **38**, 757 (1990)].

^eReference 20.

alloy. We have evaluated this quantity from published measurements of elastic constants at room temperature, assuming that dC_{II}/dT is independent of the alloy composition; this assumption is supported by present experiments in Cu-Al-Be. Results are presented in Table IV and corroborate our results for Cu-Al-Be, in the sense that A appears to be a constant magnitude at the transition temperature. The elastic anisotropy for Cu-Zn-Al is very similar to that of Cu-Al-Be and larger than the one corresponding to Cu-Al-Ni. It is worth emphasizing that these features are consistent with the behavior of ΔS , according to expressions (5) and (7).

IV. CONCLUSIONS

We have related elastic and thermal properties of Cu-based alloys undergoing a MT. The results show that (i)

values of ΔS and A at the transition temperature depend on the structure of both H and L phases, but are independent of the particular system undergoing the MT and also of its composition, and (ii) the electronic contribution to the whole entropy change appears not to be relevant in driving the MT; either its composition dependence is negligible or it contributes a very small fraction to ΔS_{tot} .

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