Entropy change of martensitic transformations in Cu-based shape-memory alloys

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We have investigated the different contributions to the entropy change at the martensitic transition of different families of Cu-based shape-memory alloys. The total entropy change has been obtained through calorimetric measurements. By measuring the evolution of the magnetic susceptibility with temperature, the entropy change associated with conduction electrons has been evaluated. The contribution of the anharmonic vibrations of the lattice has also been estimated using various parameters associated with the anharmonic behavior of these alloys, collected from the literature. The results found in the present work have been compared to values published for the martensitic transition of group-IV metals. For Cu-based alloys, both electron and anharmonic contributions have been shown to be much smaller than the overall entropy change. This finding demonstrates that the harmonic vibrations of the lattice are the most relevant contribution to the stability of the bcc phase in Cu-based alloys.

I. INTRODUCTION

Many crystalline systems show, at high temperatures, an open bcc structure and transform to a more compact close-packed structure at lower temperatures: it is the so-called martensitic transformation.[1] The transition is first order, diffusionless, and the resultant lattice distortion can mostly be described by a shear with almost no volume change.

The bcc phase is energetically unstable when compared with the close-packed structures but it is preferred by the system at high temperatures due to its large entropy resulting from low-energy vibrational transverse modes.[2] Associated with the transition, an entropy change occurs which is partially related to the change in the vibrational spectrum of the crystal. It is in this sense that these kinds of transitions have been acknowledged to be vibrational entropy driven. Following this idea, Morris and Gooding[3] have recently proposed a model in which a structural transition is only driven by the excess of vibrational entropy of the high-temperature phase. This model qualitatively reproduces some of the major features of martensitic transitions as, for example, partial softening of phonons and entropy change at the transition.

Martensitic transformations are observed in alkali metals, group-III and group-IV pure metals, noble-metal-based alloys, Ni-Ti, and Ni-Al, among other compounds. An extensively studied example of this kind of structural transition is the bcc to hcp transition in group-IV pure metals (Zr, Ti, and Hf). This transition is characterized by a static displacement corresponding to the transverse N-point phonon at wave vector $\mathbf{q}=\frac{1}{2}(110)$ with polarization vector $[1\bar{1}0]$ accompanied by a $q=0$ shear of the unit cell.[4] Phonon-dispersion curves in the bcc phase have been obtained by Petry *et al.*[5] for Ti, by Heiming *et al.*[6] for Zr and by Trapeneau *et al.*[7] for Hf. All these measurements show that the T1 $[\xi\xi 0]$ phonon branch has anomalously low frequencies. In the case of Zr and Ti, phonon-dispersion curves have also been measured in the martensitic hcp phase by Stassis *et al.*[8] The entropy change at the transition has then been obtained from the phonon density of states derived in both the bcc and hcp phases, from the measured dispersion curves.[5,6] The contribution of low-energy phonons to the total excess entropy needed to stabilize the bcc phase is 65% for Zr and 70% for Ti, while the remaining fraction has an electronic origin. In addition, these calculations showed that the vibrational entropy change contains an important anharmonic contribution. Calculations based on molecular-dynamics simulations using an N-body potential[9] and also based on first-principles anharmonic-phonon theories[10] are consistent with experimental data.

The electron contribution has been independently evaluated from the calculated electron-density of states in Ti and Zr.[11] The agreement of these values with the ones proposed in Refs. 5 and 6 is reasonable.

A number of Cu-based alloys also undergo a martensitic transition with similar features to the martensitic transition undergone by group-IV pure metals. Cu-Al and Cu-Zn are Hume-Rothery alloys. For such kinds of materials, it is known that the phase stability is controlled by the average number of valence electrons, or electrons to atom ratio (e/at.).[12] The martensitic structure exhibited by the alloys is reminiscent of the stable structure for the specific e/at. of the crystal.

Cu-based alloys have been the subject of extensive research due to their technologically important shape-memory properties.[13] Neutron-diffraction investigations have been carried out in the bcc phases of Cu-Zn-Al,[14] Cu-Al-Ni,[15] Cu-Al-Pd,[16] and Cu-Al-Be[17] alloys. They

show that the whole T1 [$\xi\xi 0$] phonon branch has very low frequencies and softens with the temperature as the transition is approached. In addition, ultrasonic measurements have shown that the elastic stiffness constant C' [$=(C_{11}-C_{12})/2$] also decreases with temperature.[18] In particular, in a previous work[19] we reported that the value of C' and the total entropy change at the transition temperature were only dependent on the structure of the low-temperature phase. This suggested that the electron contribution to the entropy change should have little influence in driving the martensitic transformation in Cu-based alloys. Verification of this idea would lead to the conclusion that in these systems the martensitic transformation is practically a pure vibrational entropy driven transition. The aim of the present paper is to confirm this issue by evaluating the electron contribution to the entropy change in Cu-based alloys. Indeed, the possibility of evaluating the different entropy contributions in metals has been a question of interest for many years and different approaches have been proposed to evaluate these terms.[11,20]

In the present work we evaluate the different contributions to the whole entropy change in families of composition-related Cu-Zn-Al, Cu-Al-Ni, and Cu-Al-Be alloys, transforming to different martensitic structures. The whole entropy change is obtained from calorimetric measurements and the electron contribution is derived from magnetic-susceptibility measurements. In addition, an estimation of the vibrational anharmonicity is also made using the sparse data available in the literature. The paper is organized as follows: in Sec. II the methods used to derive the different contributions to the entropy change are schematized. Section III deals with experiments and, finally, in Sec. IV we discuss the results obtained. Conclusions are outlined in Sec. V.

II. PRELIMINARIES

The entropy of a metal mainly stems from two different contributions, one arising from the vibrations of the lattice and the other from the conduction electrons:

$$S=S_v+S_e \ . \tag{1}$$

At moderate temperatures, electron-phonon interaction effects become negligible[21] and S_v and S_e can be obtained as follows:

$$S_v=k_B\int n_{\rm ph}(E)[(1+f_{\rm BE})\ln(1+f_{\rm BE})-f_{\rm BE}\ln f_{\rm BE}]dE \tag{2}$$

and

$$S_e=-k_B\int n_e(E)[f_{\rm FD}\ln f_{\rm FD}+(1-f_{\rm FD})\ln(1-f_{\rm FD})]dE \ , \tag{3}$$

where $n_{\rm ph}(E)$ and $n_e(E)$ are the phonon and electron density of states, respectively, and $f_{\rm BE}$ and $f_{\rm FD}$ are the Bose-Einstein and Fermi-Dirac distribution functions.

If $n_{\rm ph}(E)$ and $n_e(E)$ are known—through neutron experiments or first-principles calculations—the different contributions to the total entropy can be evaluated. Using this procedure, Eriksson, Wills, and Wallace[11] have recently obtained the electronic and quasiharmonic entropies for a number of transition metals.

For bcc Cu-based alloys, as far as we know, there are no measured data available in the literature for $n_{\rm ph}(E)$ or $n_e(E)$ and therefore, additional hypotheses are needed for the estimation of the contribution of the different terms to the stability of the bcc phase.

At temperatures of our interest, the expression in the brackets [$\cdots$] in Eq. (3) is sharply peaked near the Fermi energy. When the density of states varies slowly with E, the following approximation is obtained:

$$S_e\simeq\frac{\pi^2}{3}n(e_F)k_B^2T \ , \tag{4}$$

with $n(e_F)$, the density of states near the Fermi surface.

The density of states near the Fermi surface can be obtained from magnetic-susceptibility measurements. Let us consider the magnetic susceptibility associated with the conduction electrons of a metal. To second order in the Sommerfeld approximation, it is given by

$$\chi\simeq\left[\mu^2-\frac{1}{3}\mu'^2\right]n(e_F)\left[1-\frac{\pi^2}{12}\left[\frac{k_BT}{e_F}\right]^2\right] \ , \tag{5}$$

where μ is the intrinsic magnetic moment of the electrons, $\mu'=(m/m')\mu$, and m/m' is the ratio between free- and effective-electron masses.

Combining Eqs. (4) and (5), and neglecting terms of the order of $(k_BT/e_F)^2$, we get

$$S_e=\frac{k_B^2\pi^2T}{3\mu^2-\mu'^2}\chi \ , \tag{6}$$

i.e., the electron contribution to the entropy is proportional to the magnetic susceptibility.

Therefore, the electron entropy change at the structural phase transition is approximately given by

$$\Delta S_e=\frac{k_B^2\pi^2T}{3\mu^2-\mu'^2}\Delta\chi \ , \tag{7}$$

which provides an indirect way to obtain the electron contribution to the entropy change by measuring the magnetic susceptibility associated with conduction electrons.

This procedure can be used to evaluate, for example, the electron entropy change at the martensitic transition of Zr and Ti, which can be compared to the values obtained using the electron density of states or from the difference between the total entropy change and the vibrational entropy change. In Table I, ΔS_e values for these two metals reported in the literature[5,6,11] are compared with those obtained through magnetic-susceptibility data[22] together with Eq. (7), assuming $\mu=\mu'$. Data obtained using different methods are consistent.

The anharmonic contribution to ΔS_v can also be estimated to first-order approximation, by splitting the vibrational entropy into a purely harmonic (S_H) term plus an anharmonic (S_a) correction as follows:

$$S_v=S_H+S_a \ . \tag{8}$$

TABLE I. Entropy change associated with conduction electrons in Ti and Zr.

	Ti	Zr	
$\Delta S_e = \Delta S - \Delta S_v$ (J mol^{-1} K^{-1})	−1.08	−1.16	a
ΔS_e^{dos} (J mol^{-1} K^{-1})	−2.24	−1.41	b
ΔS_e^{χ} (J mol^{-1} K^{-1})	−1.89	−1.76	c

[a]Values obtained subtracting the vibrational contribution (ΔS_v) from the overall entropy change (ΔS). ΔS_v was calculated from phonon density of states obtained using measured dispersion curves (Ref. 6). The overall entropy change was −3.49 J mol^{-1} K^{-1} for Ti and −3.32 J mol^{-1} K^{-1} for Zr.

[b]Values obtained using electron density of states computed using the linear muffin tin orbital method (Ref. 11).

[c]Values computed using Eq. (7). We have used $\Delta\chi = -1.5\times10^{-5}$ emu mol^{-1}, $T_M = 1150$ K for Ti and $\Delta\chi = -1.4\times10^{-5}$ emu mol^{-1}, $T_M = 1150$ K for Zr (Ref. 22).

According to Grimvall,[20] a reasonable approximation to the anharmonic term at intermediate temperatures can readily be obtained by considering the difference between the heat capacities C_p and C_v; this leads to the following expression for the anharmonic contribution to the entropy at a given temperature T:

$$S_a \simeq 3k_B\gamma\beta T \ , \tag{9}$$

where γ is the thermal Grüneisen parameter and β is the volume thermal expansion.

III. EXPERIMENTAL

Different Cu-based systems have been investigated. Single crystals were grown by the modified Bridgman method. Their atomic composition and transition temperature (M_s) are given in Table II. From the original rods, samples typically 0.5–1 g were cut using a low-speed diamond saw. Calorimetric and magnetic measurements were conducted on each sample.

TABLE II. Atomic composition for the different alloys investigated.

Alloy	Composition
CZA1	$Cu_{67.7}Al_{13.0}Zn_{19.3}$
CZA2	$Cu_{67.9}Al_{15.9}Zn_{16.2}$
CZA3	$Cu_{69.5}Al_{20.5}Zn_{10.0}$
CZA4	$Cu_{69.7}Al_{23.1}Zn_{7.2}$
CAN1	$Cu_{68.9}Al_{27.3}Ni_{3.8}$
CAN2	$Cu_{68.4}Al_{27.8}Ni_{3.8}$
CAN3	$Cu_{67.9}Al_{28.3}Ni_{3.8}$
CAN4	$Cu_{67.4}Al_{28.8}Ni_{3.8}$
CAB1	$Cu_{74.3}Al_{22.8}Be_{2.9}$
CAB2	$Cu_{73.7}Al_{22.7}Be_{3.6}$

Cu-Zn-Al alloys have been selected with a different number of electrons per atom (e/at.). For high e/at. (≥ 1.51), the transformation is toward a hexagonal ($2H$) structure while for e/at. between 1.45 and 1.51, the transformation is toward an orthorhombic ($18R$) structure. Cu-Al-Ni and Cu-Al-Be samples have approximately the same e/at. Cu-Al-Be samples transform to an $18R$ structure and Cu-Al-Ni samples to a $2H$, except for sample CAN1 which transforms to a mixture of $2H$ and $18R$ phases. In this case, the presence of the $18R$ phase is due to the internal stresses generated with the development of the $2H$ phase (see phase diagram in Ref. 23). The same thing also applies for sample CZA3.

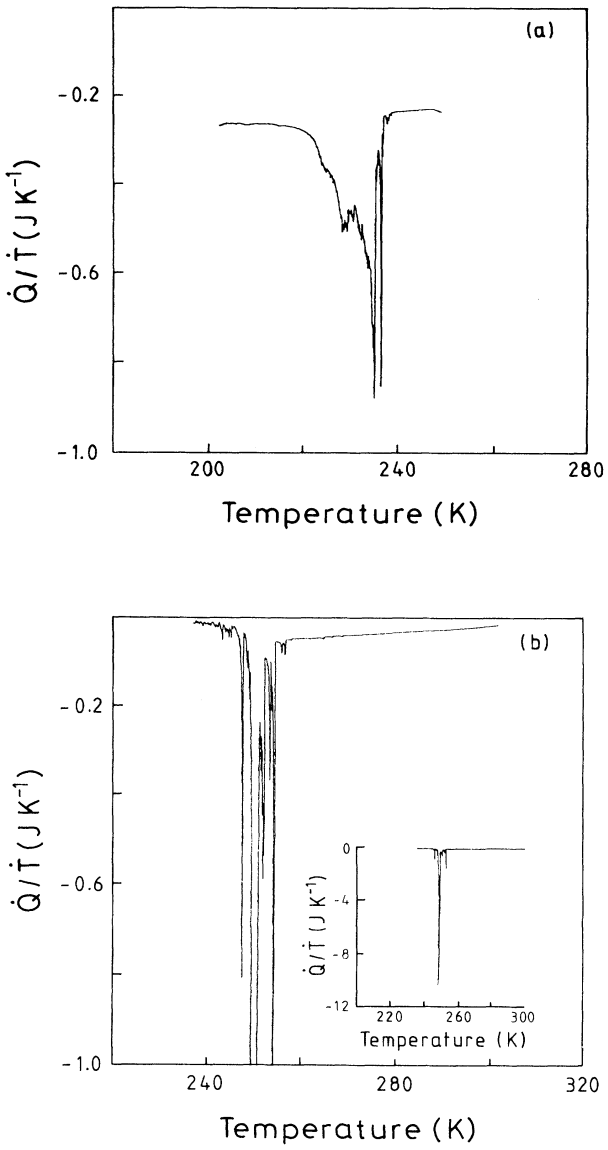

FIG. 1. Typical thermal curves for a bcc→$18R$ (a) and for a bcc→$2H$ (b) transitions in Cu-Zn-Al alloys. [(a) corresponds to sample CZA2 and (b) to sample CZA4]. In the inset of (b) the thermal curve for the bcc→$2H$ transition is plotted in full.

A. Calorimetric measurements

Differential-scanning-calorimetry measurements have been conducted using a high-sensitivity microcalorimeter, described elsewhere.[24] Temperature scans range between 100–300 K and have been performed at rates around 1 K min^{-1}. It is worth noticing that the entropy change at the martensitic transformation of Cu-based alloys is relatively small, around 1.5 J mol^{-1} and therefore high accuracy is required in order to obtain reliable data.

In Fig. 1 we show two typical thermal curves corresponding to a bcc→18R (a) and to a bcc→2H (b) transformation for Cu-Zn-Al alloys. Notice the different kinetic features between the two transitions; the transition toward 2H is always jerkier and with a larger thermal hysteresis (~30 K, not shown in the figure) than the transition towards 18R (typical hysteresis ~10 K). This fact has already been reported.[25]

Transition temperatures, heats exchanged, and entropy changes are obtained from the recorded thermal curves. Details for the data treatment can be found in Ref. 26. The values obtained for all the alloys are given in Table III, together with the martensite start (M_s) and reverse finish (A_f) temperatures.

An interesting feature arising from the data presented in Table III is the constancy in the entropy change of the transition (ΔS) for all samples transforming to the same martensitic structure, independent of the alloy system and of the specific composition. Alloys transforming to 2H martensite (samples CZA3, CZA4, CAN2, CAN3, and CAN4) have a value for ΔS slightly larger than those transforming to 18R martensite; average values are

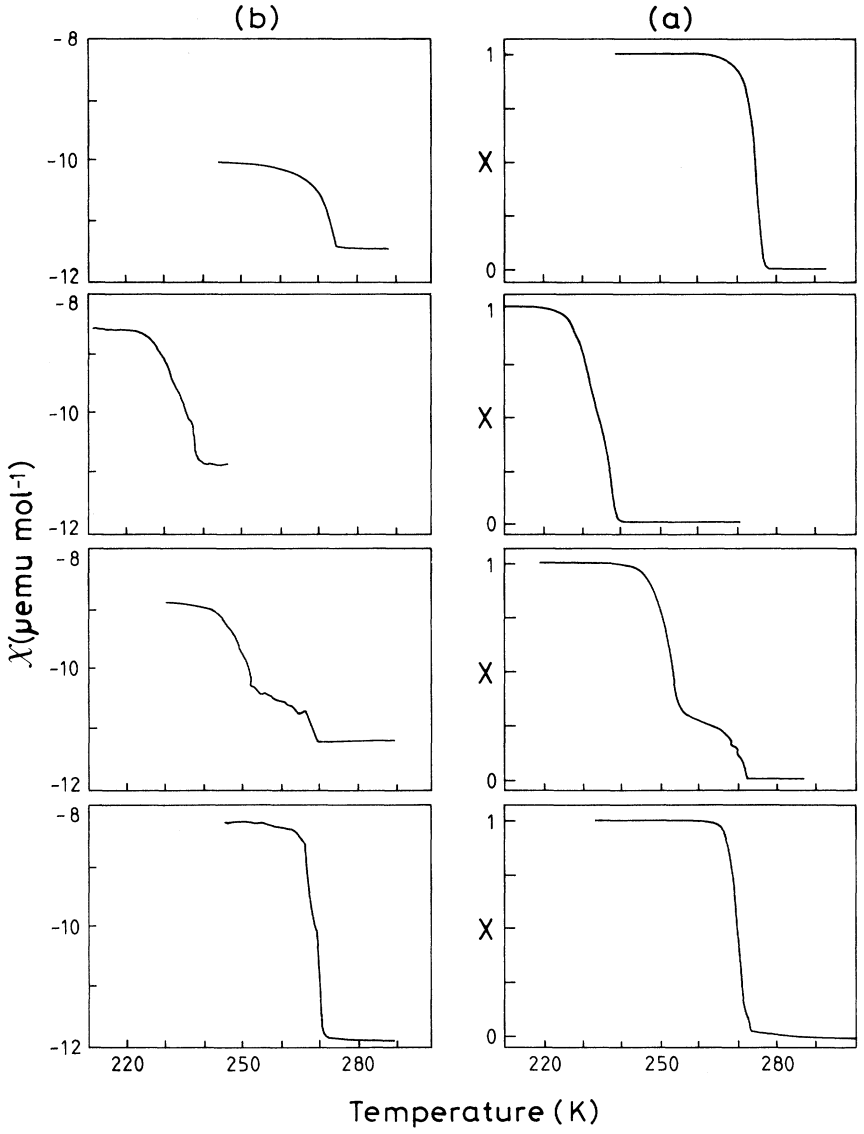

FIG. 2. Transformed fraction (a) and magnetic susceptibility (b) as a function of temperature during the reverse martensitic transition of Cu-Zn-Al alloys.

TABLE III. Martensitic start (M_s) and reverse finish (A_f) temperatures, heats exchanged Q, and entropy change $\Delta S(=S^m-S^{bcc})$, for all the investigated alloys. Estimated experimental uncertainties are ± 1 K for the transformation temperatures, less than 5% for the heat exchanged and around 5% for the entropy change.

Alloy	M_s (K)	A_f (K)	Q (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
CZA1	274	276	−382	−1.42
CZA2	239	242	−335	−1.47
CZA3	254	272	−377	−1.55
CZA4	267	275	−382	−1.51
CAN1	284	322	−407	−1.46
CAN2	242	281	−371	−1.54
CAN3	188	224	−303	−1.61
CAN4	151	180	−227	−1.50
CAB1	227	236	−297	−1.40
CAB2	145	152	−198	−1.44

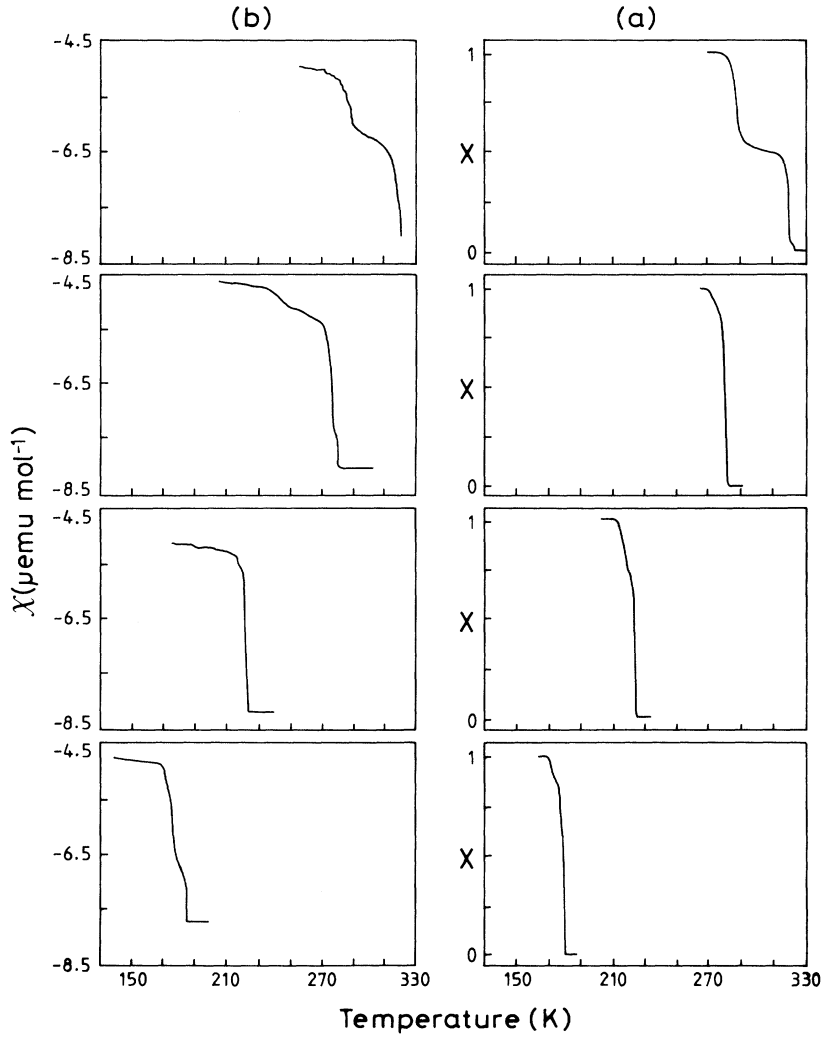

FIG. 3. Transformed fraction (a) and magnetic susceptibility (b) as a function of temperature during the reverse martensitic transition of Cu-Al-Ni alloys.

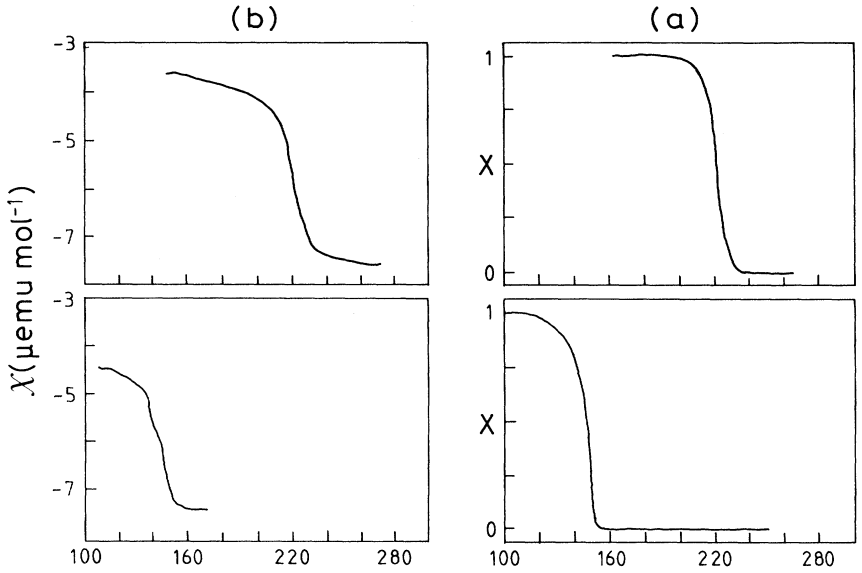

FIG. 4. Transformed fraction (a) and magnetic susceptibility (b) as a function of temperature during the reverse martensitic transition of Cu-Al-Be alloys.

$\Delta S^{bcc\rightarrow 2H} = -1.54\pm0.04$ J mol^{-1}K^{-1} and $\Delta S^{bcc\rightarrow 18R} = -1.44\pm0.03$ J mol^{-1}K^{-1}. Present data (which have been extended to different alloy systems) corroborate the conclusions that we have already stressed in a previous work.[19]

The extensiveness of the entropy enables computation of the volume fraction transformed at each temperature, $x(T)$. Figures 2(a), 3(a), and 4(a) show this parameter for the reverse transformations of Cu-Zn-Al, Cu-Al-Ni, and Cu-Al-Be alloys, respectively.

B. Magnetic measurements

DC susceptibility measurements were performed by using a commercial superconducting quantum interferencial device (SQUID) magnetometer equipped with second-order gradiometer pickup coils in applied magnetic fields around 2 T and temperatures between 100 K and room temperature.

The evolution of the magnetic susceptibility with temperature in the heating up processes is shown in Figs. 2(b), 3(b), and 4(b) for Cu-Zn-Al, Cu-Al-Ni, and Cu-Al-Be alloys, respectively. A small discontinuity is observed at the temperatures where the transition takes place. The high sensitivity of SQUID magnetometers enables computation of the magnitude of this discontinuity $\Delta\chi$ with enough accuracy. $\Delta\chi$ has been evaluated from the recorded curves and is given in Table IV. The table also gives the transition temperature T_M for all the alloys. The excellent agreement between T_M and A_f measured calorimetrically is worth noticing.

Sample CAN1 has a finish reverse transformation temperature of 322 K (see Table III) which falls slightly above the upper limit of operation of our SQUID. For this sample, we have evaluated $\Delta\chi$ using the proportionality between this magnitude and the transformed fraction $x(T)$, which will be discussed in the following section.

Cu-Zn-Al alloys have been chosen to have a different number of electrons per atom (e/at.). Such a difference is reflected by the different values obtained for $\Delta\chi$. In Fig. 5, $\Delta\chi$ is plotted as a function of e/at.; the increase of $\Delta\chi$ with e/at. is rather linear.

In order to check for any possible magnetic anisotropy effect associated with the single-crystalline nature of the samples we have performed several measurements on some specific samples with the magnetic field applied in different crystallographic directions. Results obtained were similar and confirm that the magnetic-susceptibility jump does not depend on the direction of the applied magnetic field.

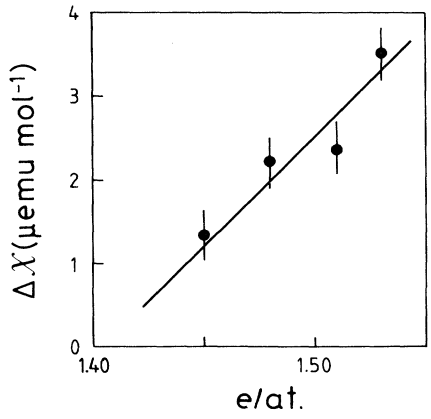

FIG. 5. Change in the magnetic susceptibility at the transition, for different electron per atom ratios (e/at.) in Cu-Zn-Al alloys.

IV. DISCUSSION

From Figs. 2(b), 3(b), and 4(b) it is apparent that the magnetic susceptibility for Cu-based alloys is negative; i.e., these alloys are diamagnetic in both the bcc and martensitic phases. Evaluation of ionic diamagnetism for Cu-Zn-Al, Cu-Al-Ni, and Cu-Al-Be from values of the ions in the corresponding pure metals renders ionic contributions ranging between -10^{-5} and -10^{-6} emu mol^{-1}, which are close to those found in our samples and accrue for the main contribution to the magnetic susceptibility in these alloys.

Due to the diffusionless nature of the martensitic transformation, the neighbors of any given atom remain neighbors during and after the transition, thus implying that the alloy behaves as a one-component solid during the transition.[12] As a consequence of this, no change in the ion diamagnetism is expected at the transition and, in this sense, Cu-based alloys are comparable to pure metals for which the change in the magnetic susceptibility at the phase transition is associated with conduction electrons. Such fact is validated by the excellent proportionality existing between $\Delta\chi(T)$ and the transformed fraction $x(T)$, exemplified in Fig. 6.

The composition for Cu-Al-Ni and Cu-Al-Be alloys does not change appreciably from one sample to the other and e/at. is almost constant, but the change in M_s is substantial; on the contrary, M_s for all Cu-Zn-Al alloys is similar (except for sample CZA2). Present measurements of $\Delta\chi$ show that this magnitude exhibits a linear dependence with e/at. but does not exhibit a systematic dependence with the transition temperature.

A feature arising from Figs. 2(b), 3(b), and 4(b), and from the values in Table IV is the small value of $\Delta\chi$ ($\sim 10^{-6}$ emu mol^{-1}). Such a small value results in very small values for the electron contribution to the entropy change, obtained from Eq. (7), and assuming $\mu=\mu'$. Values for all the alloys investigated are given in Table V. In order to estimate the validity of the approximation $\mu=\mu'$ we have independently evaluated m' from low-temperature specific-heat measurements reported by Abbé, Caudron, and Pynn[27] for a family of Cu-Zn-Al alloys with e/at. ranging from 1.46 to 1.53. For all the alloys the values are very similar, centered at $m/m' \approx 0.6$. This correction would result in values smaller by less than 20% than those given in Table V. This modification is not relevant for present purposes and will not be further considered.

ΔS_e for Cu-based alloys are in absolute values, one order of magnitude smaller than those found for Zr and Ti (see Table I). Another important fact is that ΔS_e for Cu-based alloys is positive, contrary to what happens in Zr and Ti. This finding means that, in Cu-based alloys, the

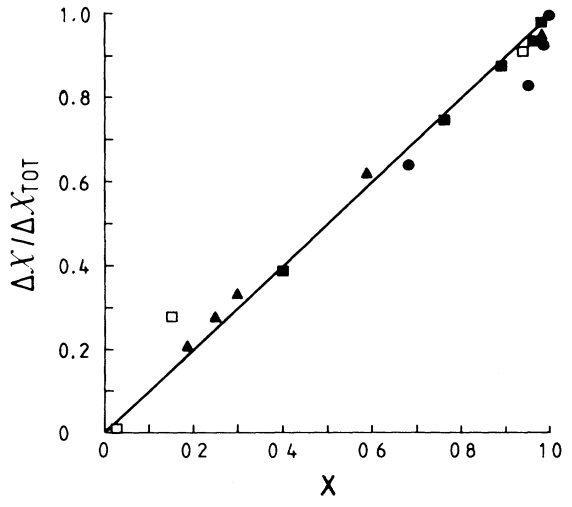

FIG. 6. Normalized change in the magnetic susceptibility as a function of the transformed fraction, for the four Cu-Zn-Al alloys. Data have been sampled every 5 K, in each case. CZA1 (■), CZA2 (□), CZA3 (▲), CZA4 (●).

TABLE IV. Magnetic-susceptibility discontinuity $\Delta\chi$ and transition temperature T_M for all the alloys investigated. Estimated experimental uncertainties are ±2 K for the transition temperatures and around 6% for the magnetic-susceptibility discontinuity.

Alloy	$\Delta\chi$ ($\times 10^{-7}$) (emu mol^{-1})	T_M (K)
CZA1	13.7	274
CZA2	22.2	240
CZA3	23.4	270
CZA4	35.3	271
CAN1	29.7[a]	
CAN2	32.8	278
CAN3	28.1	224
CAN4	28.1	185
CAB1	35.7	240
CAB2	30.0	156

[a]Evaluated taking into account the proportionality between the relative change in magnetic susceptibility and the transformed fraction (see text for details).

TABLE V. Electron contribution to the entropy change for different Cu-based alloys.

Alloy	ΔS_e ($\times 10^{-2}$) (J mol^{-1} K^{-1})
CZA1	4.1
CZA2	5.9
CZA3	6.9
CZA4	10.5
CAN1	8.8
CAN2	10.0
CAN3	6.9
CAN4	5.7
CAB1	10.6
CAB2	8.9

entropy associated with conduction electrons stabilizes the martensitic phase instead of stabilizing the bcc phase, as occurs in group-IV pure metals. The low values found for ΔS_e in the present work enable us to state that the overall entropy change ΔS in Cu-based alloys is dominated by the lattice vibration contribution ΔS_v. Results for Cu-Zn-Al show that ΔS_e increases with the electron density e/at. as it is displayed in Fig. 7. ΔS also depends on e/at. and a dependency of ΔS with e/at. has very recently been reported.[28] Figure 7 shows that this fact is mainly due to the dependence of ΔS_v with e/at. For samples with constant e/at., ΔS_e exhibits a composition dependence that parallels that of the transition temperature T_M, which results from the fact that $\Delta\chi$ is composition independent within our experimental uncertainty. In a previous work we have reported ΔS for a large number of samples with the same e/at.[19] These results indicated that ΔS is, within the experimental error, composition independent. Thus, taking into account that ΔS_e is very small, a possible but very weak dependence of ΔS_v with composition could be expected.

We can finally attempt to separate the contribution of the anharmonic vibrations from that of the harmonic vibrations. Unfortunately, there are almost no data available for the anharmonic behavior of Cu-based alloys. We have estimated ΔS_a using Eq. (9) and the following available information. Recent measurements of the vibrational anharmonicity have been performed by Jurado *et al.*[29] in the bcc phase of a Cu-Al-Be single crystal. For this crystal, the thermal Grüneisen parameter γ is 1.5 and the volume thermal expansion β is 4.47×10^{-5} K^{-1}. Data for the martensitic phase are still more sparse. We have used the following values to compute the thermal Grüneisen parameter $\gamma[=(\beta B/\rho C_p)]$: the volume thermal expansion of α-brass ($3R$ structure) $\beta=5\times10^{-5}$ K^{-1},[30] the heat capacity of $18R$ Cu-Zn-Al, $C_p=0.407$ J g^{-1} K^{-1},[31] the density $\rho=7589$ kg m^{-3}, and the bulk modulus $B=102$ GPa calculated from very recent measurements of all the elastic constants in an $18R$ Cu-Zn-Al single crystal.[32] With all these data we have estimated that the anharmonic contribution to the entropy change at a typical temperature of 300 K will be around $\Delta S_a\approx0.1$ J K^{-1} mol^{-1}. This value is less than 10% of the overall entropy change. Notice that the anharmonic contribution is larger in martensite than in the bcc phase. The anharmonicity of the low-energy modes is expected to be larger in the bcc phase than in the close-packed phase, with a marked tendency to increase as the transition is approached. Nevertheless, these soft modes are only a small fraction of the vibrational modes of the crystal and the contribution of the remaining modes can counterbalance the effect of soft modes in the overall anharmonic entropy change contribution. Indeed, recent measurements of the anharmonic behavior of the long-wavelength acoustic modes[29] in the bcc phase have shown that the anharmonicity of the modes associated with C' increases approaching the transition, but the anharmonicity of all longitudinal modes decreases with temperature. In any case, the order of magnitude found for ΔS_a in the present work enables us to conclude that the anharmonic contribution to the entropy will not be a relevant term in stabilizing the bcc phase in Cu-based alloys.

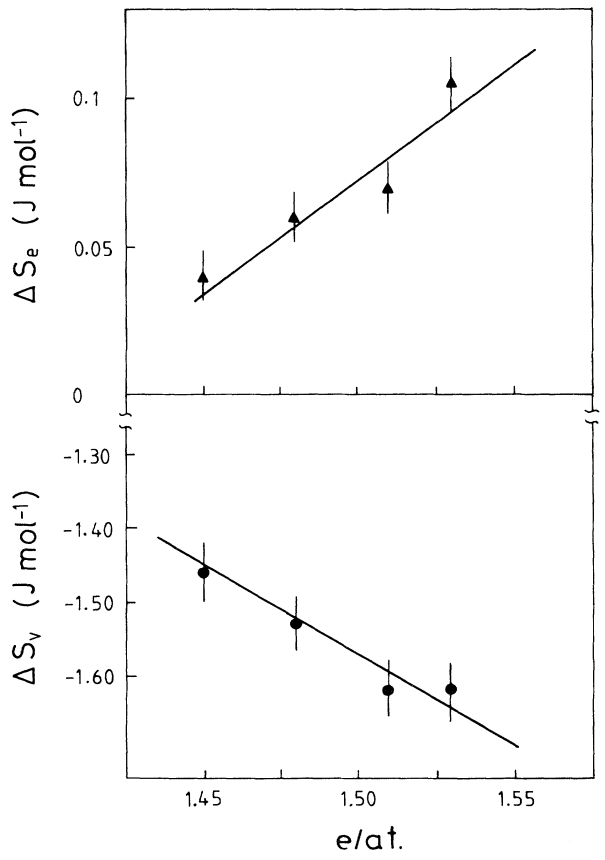

FIG. 7. Vibrational and electronic contribution to ΔS as a function of e/at. for Cu-Zn-Al alloys.

V. CONCLUSIONS

We have evaluated the different contributions to the entropy change at the martensitic transition of Cu-based shape memory alloys. The entropy associated with conduction electrons is larger in the close-packed phase than in the bcc phase, and is a stabilizing factor for the martensitic phase but the magnitude of its change at the transition amounts less than 10% of the overall entropy change. A rough estimation of the anharmonic vibrational entropy has rendered a value which is also less than 10% of the overall entropy change. We have thus established that the overall entropy change at the martensitic transition of Cu-based alloys stems mainly from the harmonic vibrations of the lattice. Thus we can state that the martensitic transformation in Cu-based alloys is practically a pure vibrational entropy driven transition.

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