

## Rapid Communications

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### Influence of configurational atomic order on the relative stability of bcc and close-packed structures in Cu-based alloys

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We present a study of the influence of atomic order on the relative stability of the bcc and the 18R martensitic structures in a  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$  crystal. Calorimetric measurements have shown that disorder increases the stability of the 18R phase, contrary to what happens in Cu-Zn-Al alloys for which it is the bcc phase that is stabilized by disordering the system. This different behavior has been explained in terms of a model recently reported. We have also proved that the entropy change at the martensitic transition is independent of the state of atomic order of the crystal, as predicted theoretically. Our results suggest that differences in the vibrational spectrum of the crystal due to different states of atomic order must be equal in the bcc and in the close-packed phases.

The stability of the bcc phases exhibited at high temperatures by some metals and alloys stems from the fact that they have an entropy larger than the entropy of the close-packed structures that would be the stable phases from purely energetic considerations.<sup>1</sup> Most of these metals and alloys undergo a structural transition towards a close-packed structure at a temperature  $M_s$ . This is the so-called martensitic transition which is first order, diffusionless, and is mainly accomplished by a homogeneous (110)  $\langle 1\bar{1}0 \rangle$  shear.<sup>2</sup>

Phonon softening has been observed on approaching the transition: both the frequencies of the low-energy  $T_2$  transverse  $[\xi\xi 0]$  phonons<sup>3</sup> and the shear elastic constant  $C'$  [ $= (C_{11} - C_{12})/2$ ] (Ref. 4) decrease with temperature. An entropy change occurs at the transition, related to the change in the vibrational spectrum of the crystal; it is in this sense that these transitions have been acknowledged to be vibrational-entropy driven. Indeed, extensive research dealing with the role played by vibrational entropy in driving the martensitic transition is being undertaken from both experimental<sup>4-6</sup> and theoretical<sup>7</sup> points of view.

On the other hand, most of the alloys undergoing martensitic transitions exhibit ordered structures below a certain temperature  $T_c$  ( $T_c > M_s$ ). There has been rapid progress towards understanding the thermodynamics of atomic order in metals and alloys, but there is only very weak experimental evidence for the importance of vibrational entropy in order-disorder transformations. For example, only very recently has this effect been estimated for Ni-Al alloys.<sup>8</sup>

Since it is established that the degree of atomic order modifies the relative stability of the bcc and the close-packed structures,<sup>9</sup> an investigation of the influence of atomic order on the martensitic transition will provide valuable information about order-disorder processes and martensitic transitions, both topics of great interest nowadays.

In the present work we have studied a shape-memory Cu-Al-Be alloy close to a stoichiometric  $\text{Cu}_3\text{Al}$  composition. This alloy undergoes an order-disorder transition from a disordered ( $Im\bar{3}m$ ) to an  $L2_1$  ordered ( $Fm\bar{3}m$ ) structure and a martensitic transformation from a bcc to an orthorhombic (18R) structure. It has been established that for this alloy, the martensitic transition is purely vibrational-entropy driven.<sup>6</sup> The sample investigated is a single crystal ( $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$ ) grown by a modified Bridgman method (0.689 g) with transition temperatures  $T_c \approx 800$  (Ref. 10) and  $M_s \approx 240$  K (Ref. 4) for the order-disorder and martensitic transitions, respectively. We have established different degrees of atomic order in the crystal by means of the following heat treatments. First the sample is maintained at 973 K for 300 s, then it is air cooled down to a temperature  $T_q$  (characteristic cooling time about 300 s) and when this temperature is reached, it is quenched into a mixture of ice and water. This heat treatment is suitable to have the sample at  $T_q$  with its equilibrium ordering degree.<sup>11</sup> Just after the quench, the martensitic transition has been investigated using a high-sensitivity microcalorimeter.<sup>12</sup> A second calorimetric run has been performed 23 h after the first run. Both sets of data are compared to those obtained after a reference

heat treatment consisting of an air cooling from 973 K down to room temperature, for which a maximum degree of atomic order is expected.

In Fig. 1 we present some typical curves obtained for the bcc $\rightarrow$ 18R transition just after a quench from different  $T_q$  temperatures (a) and after a 23 h room-temperature aging (b). It is apparent from the curves that the martensitic transition takes place at different temperatures for different  $T_q$ . In addition the kinetics of the transition is also dependent on  $T_q$ : the jerky character of the transition depends on  $T_q$  and premonitory effects are detected above the bulk of the transformation. The magnitude of these phenomena is maximum for  $T_q$  around 820 K. After 23 h room-temperature aging there is a slight change in the transition temperatures, the transformation is less jerky and the premonitory effects are almost undetectable.

In order to quantify the change in the transition temperature with  $T_q$  we have adopted the temperature of the maximum of the thermal curve ( $T_M$ ) as a signature for the equilibrium temperature between bcc and 18R phases.  $T_M$  is plotted in Fig. 2 as a function of  $T_q$ . After 23 h room-temperature aging,  $T_M$  is always slightly lower than just after the quench but it exhibits the same dependence with  $T_q$ , indicating that changes in  $T_M$  have a different origin than the jerky character of the transition together with the presence of premonitory effects. These

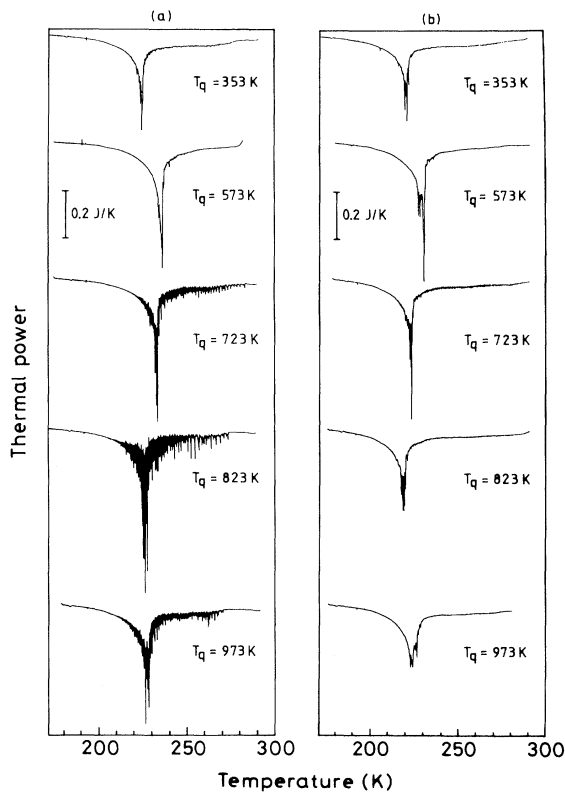


FIG. 1. Typical thermal curves obtained during the bcc $\rightarrow$ 18R transition of  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$  just after the quench (a) and after 23 h room-temperature aging (b) for different quenching temperatures  $T_q$ .

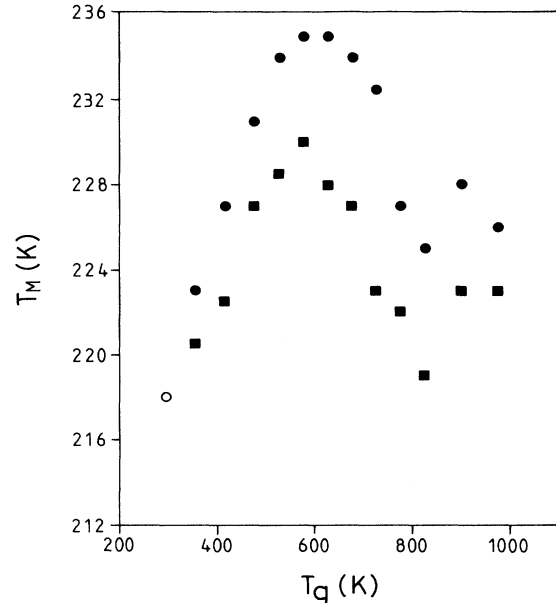


FIG. 2. Transition temperature ( $T_M$ ) as a function of quenching temperature  $T_q$  for  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$  (●): Just after a quench; (■): after 23 h room-temperature aging. The open circle corresponds to a standard heat treatment.

two last phenomena are associated to a large number of quenched-in vacancies that act as pinning centers for the motion of the interfaces. After 23 h room-temperature aging most of the vacancies are eliminated and as a consequence these effects have considerably decreased in magnitude.

It is worth mentioning that premonitory effects of tweed nature have been detected in a number of systems undergoing martensitic transitions<sup>13</sup> and have been attributed to compositional random disorder of thermal origin.<sup>14</sup> We believe that the premonitory effects observed here are also associated to random disorder, nevertheless optical microscopy observations have shown that these effects, detected calorimetrically, are related to the transition of domains with length scales comparable to those transforming at the bulk of the transformation.

Changes in  $T_M$  with  $T_q$  are due to different degrees of atomic order reached by the system. Recently a model has been proposed<sup>15</sup> that accounts for changes in the martensitic transition temperature in terms of the degree of atomic order and the pair ordering energies of the different atomic elements. This model also predicts the entropy change at the martensitic transition to be independent of the degree of atomic order.

The dependence of the transition temperature with the long-range atomic order parameter  $s$  can be expressed as<sup>15</sup>

$$\Delta M_s \cong (1/\Delta S)K[s^2(T_q) - s_0^2], \quad (1)$$

where  $s_0$  and  $s(T_q)$  are the equilibrium values of the long-range atomic order parameter at room temperature and  $T_q$ , respectively.  $\Delta S$  is the entropy change at the martensitic transition. The parameter  $K$  is related to pair ordering energies as

$$K = \frac{2}{3} W^{(1)} - V^{(2)}. \quad (2)$$

For our Cu-Al-Be alloy, the composition is close to stoichiometric  $\text{Cu}_3\text{Al}$  and  $W^{(1)}$  is taken to be the nearest-neighbor ordering energy for Cu-Al pairs in the martensitic phase and  $V^{(2)}$  to be the next-nearest-neighbor ordering energy for Cu-Al pairs in the bcc phase.

Using the pair ordering energies given in Refs. 9 and 11,  $W^{(1)}=1250$  K and  $V^{(2)}=825$  K, and taking  $\Delta S=0.16k_B$  we obtain a maximum shift in the martensitic transformation temperature of 50 K.

A dependence of  $M_s$  with ordering has already been reported for Cu-Zn-Al alloys.<sup>16</sup> It has been shown that for this system, the configurational atomic order tends to stabilize the bcc phase. In particular we have examined a  $\text{Cu}_{2.72}\text{Zn}_{0.64}\text{Al}_{0.64}$  single crystal under the same experimental conditions as for  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$ . Results are shown in Fig. 3. They are in agreement with those reported previously.<sup>11</sup> In this case, the absence of detectable premonitory effects enables an accurate determination of  $M_s$ .

We have estimated the maximum shift predicted theoretically for  $\text{Cu}_{2.72}\text{Zn}_{0.64}\text{Al}_{0.64}$  using the pair ordering energies given in Refs. 9 and 11 and  $\Delta S=0.16k_B$ . For this alloy  $W^{(1)}$  and  $W^{(2)}$  are given by

$$W^{(1)} = (x_{\text{Zn}} W_{\text{Cu-Zn}}^{(1)} + x_{\text{Al}} W_{\text{Cu-Al}}^{(1)}) / (x_{\text{Al}} + x_{\text{Zn}}), \quad (3)$$

$$V^{(2)} = (x_{\text{Zn}} V_{\text{Cu-Zn}}^{(2)} + x_{\text{Al}} V_{\text{Cu-Al}}^{(2)}) / (x_{\text{Al}} + x_{\text{Zn}}) \quad (4)$$

with  $V_{i-j}^{(2)}$  and  $W_{i-j}^{(1)}$  the ordering energies for  $i$ - $j$  pairs and  $x_i$ , the atomic fraction of the  $i$  component ( $i, j = \text{Cu, Zn, Al}$ ). We have obtained a maximum shift in  $M_s$  of  $-68$  K.

It is worth noting that the model predicts an increase

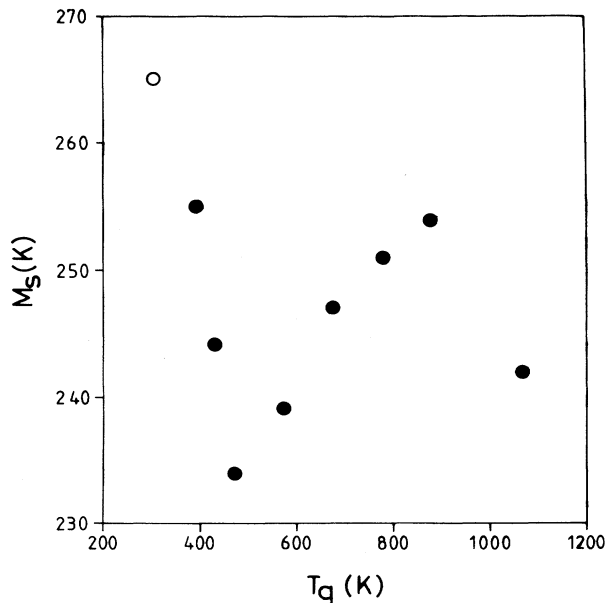


FIG. 3. Transition temperature ( $M_s$ ) as a function of quenching temperature  $T_q$  for  $\text{Cu}_{2.72}\text{Zn}_{0.64}\text{Al}_{0.64}$ , measured just after a quench. The open circle corresponds to a standard heat treatment.

in the transition temperature for  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$  and a decrease for  $\text{Cu}_{2.72}\text{Zn}_{0.64}\text{Al}_{0.64}$ , in perfect agreement with experimental findings. The predicted shifts are larger than the measured ones; in fact, the model only gives an upper limit for the transition temperature shift owing to the fact that it cannot account for the partial reordering of the system that takes place during the quench, which is experimentally unavoidable because real quenches are performed at high but finite cooling rates.

As displayed in Fig. 2,  $T_M$  (or  $M_s$ ) does not exhibit a monotonous dependence with  $T_q$ , the  $T_M$  (or  $M_s$ ) versus  $T_q$  curve has a minimum for  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$  and a maximum for  $\text{Cu}_{2.72}\text{Zn}_{0.64}\text{Al}_{0.64}$  at  $T_q \approx 820$  K. These extrema are associated with the fact that the order-disorder transition is around this value for the two alloys and therefore maximum reordering is expected for quenches from around this temperature.

From the recorded thermal curves, we have computed the entropy change ( $\Delta S$ ) for the transition undergone after 23 h room-temperature aging. The reason for choosing the second cycle is that the effect of atomic order is separated from other spurious effects such as interface pinning at vacancies that may result in irreversible energy dissipation, leading to entropy production. The results obtained for  $\Delta S$  are plotted in Fig. 4 as a function of  $T_q$ ; the constancy of  $\Delta S$  is remarkable (scatter less than 3%), with an average value of  $0.154 \pm 0.003k_B$ . It has been shown that for displacive transitions undergone by systems with a high elastic anisotropy, the equivalence between a shear in a (110) plane along the  $\langle 1\bar{1}0 \rangle$  and along the  $\langle \bar{1}10 \rangle$  directions, leads to an entropy change between the bcc and the close-packed phases independent of the degree of atomic order.<sup>15</sup> This theoretical prediction is confirmed by present results in  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$ .

Recent neutron-scattering measurements in bcc  $\text{Fe}_3\text{Al}$  (Ref. 17) have shown that only the soft  $T_2$  transverse  $[\xi\xi 0]$  mode is affected by the state of order in the crystal. A decrease of 0.50 THz in the zone boundary frequency from the disordered to the ordered ( $\text{DO}_3$ ) structures has been measured. This value enables computation of the entropy difference between disordered and ordered structures to be around  $0.4k_B$ . On the other hand, the excess vibrational entropy between disordered and ordered ( $L_2$ ) structures has only very recently been measured for

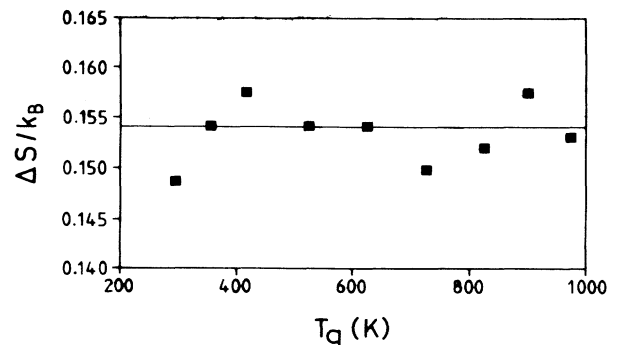


FIG. 4. Entropy change computed for the martensitic transition undergone by  $\text{Cu}_{2.96}\text{Al}_{0.92}\text{Be}_{0.12}$  after 23 h room-temperature aging.

the close-packed fcc Ni<sub>3</sub>Al to be  $0.3 \pm 0.1 k_B$ .<sup>8</sup> The excess vibrational entropy of the disordered phase is equal in the two alloys within experimental uncertainties. Even if these results correspond to different alloy systems, they suggest that the entropy difference between the bcc and the close-packed structures phases should not be dependent on the state of order, thus the constancy in  $\Delta S$  found in Cu<sub>2.96</sub>Al<sub>0.92</sub>Be<sub>0.12</sub> may have a very general character.

In conclusion, we have investigated the effect of atomic order on the martensitic transition of Cu-based shape memory alloys. The degree of atomic order modifies the relative stability between bcc and 18R phases; the change

in the equilibrium temperature can be accounted for in terms of the pair ordering energies of the elements. The entropy change at the transition does not depend on the state of order of the system: should an entropy difference between ordered and disordered states exist in the bcc phase, this difference is maintained in the close-packed phase.

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