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THE MARTENSITIC TRANSFORMATION IN β Cu-Zn*

W. ARNEODO† and M. AHLERS‡

The stress dependence of the start temperature for the martensitic transformation has been measured for single crystals of 39.2–40.4 at.% Zn deformed in tension and in compression. The entropy change ΔS is found to be independent of crystal orientation and composition; its value is $\Delta S = 0.31 \pm 0.01$ cal/mol deg. The critical shear stress to induce the "memory" type plastic deformation in the martensitic single crystals has also been measured and the stacking fault energy Γ has been deduced. Γ depends strongly on the zinc concentration. Using the experimentally determined ΔS and Γ, the stability of the martensitic phase is discussed.

LA TRANSFORMATION MARTENSITIQUE DANS β CU-ZN

La dépendance sur contrainte de la température pour commencer la transformation martensitique a été mesurée pour des monocristaux de 39,2–40,4 at.% Zn deformés en traction et en compression. Les auteurs trouvent que le changement d'entropie ΔS est indépendent de l'orientation et de la composition du cristal; sa valeur est égale à $\Delta S = 0,31 \pm 0,01$ cal/mol degré. La cission critique pour produire le genre de déformation plastique "mémoire" dans les monocristaux martensitiques a été également mesurée, et l'énergie de défaut d'empilement, Γ, a été déduite. Γ dépend fortement sur la concentration du zinc. En utilisant les valeurs expérimentaux de ΔS et de Γ, la stabilité de la phase martensitique est discutée.

MARTENSITISCHE UMWANDLUNG IN β-Cu-Zn

Die Spannungsabhängigkeit der Starttemperatur der martensitischen Umwandlung wurde an zug- und druckverformten Einkristallen mit 39,2 bis 40,4 At.% Zn gemessen. Die Entropieänderung ΔS ist unabhängig von Kristallorientierung und Zusammensetzung: $\Delta S = 0,31 \pm 0,01$ cal/Mol. Grad. Auch die kritische Schubspannung für eine "bleibende" plastische Verformung in den Martensiteinkristallen wurde gemessen und daraus die Stapelfehlerenergie Γ abgeleitet. Γ hängt stark von der Zinkkonzentration ab. Anhand der experimentellen Werte ΔS und Γ wird die Stabilität der martensitischen Phase diskutiert.

INTRODUCTION

The temperature M_s at which martensite forms in β Cu–Zn is strongly dependent on the concentration of the alloying elements.(1) It had been shown recently(2) that the factor which controls M_s in the binary β Cu–Zn some ternary alloys based on the Cu–Zn system is the tetragonality of the faulted face centered martensite lattice. It is generally assumed that ΔS can be measured from the stress dependence of the transformation temperature and investigations with the Au–Cd(3) and In–Tl(4) system indeed have shown that the critical shear stress σ_M to induce the martensite is linearly dependent on $M_s(\sigma_M)$ and that the heat of transformation calculated from ΔS agrees well with the value obtained by calorimetry. However, the martensite transformation involves also shears on others than the habit plane, and it has not yet been proved that the external stresses do no influence these shears, leading to an additional stress dependence of M_s. This would imply that ΔS depends on the crystal orientation, and that the variant which is induced is not necessarily the one with the highest shear stress component parallel to the martensite shear. One aim of this paper is to demonstrate how reliable the measurements for ΔS are and to determine the concentration dependence of ΔS.

Another important parameter which characterizes the stability of the martensite is the stacking fault energy Γ of the faulted face centered structure. It had been shown(5) that the "memory type" plastic deformation of the martensite phase is due to the movement of partial dislocations. Thus by measuring the critical shear stress for this process it should be possible to obtain information on Γ; the results are reported in this paper.

EXPERIMENTAL PROCEDURES

Weighed quantities of 99.999% copper and zinc were melted in sealed vycor tubes, and cylindrical single crystals were grown by the Bridgman technique, annealed for 6 hr at 850°C and quenched into ice water. The compositions ranged from 39.2 to 40.6 at.% Zn: 39.2 at.% Zn is near the lowest limit for obtaining single crystals without precipitates of the α-phase; in alloys with more than 40.6 at.% Zn M_s is too low to make measurements above the temperature of liquid nitrogen. In order to eliminate surface irregularities the samples were first spark-machined and then electropolished. The samples that were used for compression had a diameter of 3–4 mm and a length of 10 mm. The samples for tensile deformation were spark-machined only at their center parts, in this way the thicker ends could be fitted into grips. The center part had a length of about 40 mm and a

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diameter between 1.5 and 3 mm. The single crystals were deformed in an Instron table model deformation machine at temperatures between −80°C and liquid nitrogen (−196°C). The temperature of the samples during the deformation was measured by a copper–constantan thermocouple. In order to observe the surface markings associated with the transformation and to determine their orientation, a low temperature optical stage was built. In this stage a sample could be studied between room temperature and −196°C while being under a compressive or tensile stress. The stressed samples could be rotated around their axes and the inclination of the surface traces could be measured.

RESULTS

In Fig. 1 is shown a stress–strain curve obtained during a loading and unloading cycle in compression. The transformation starts at a critical stress σ_M and continues at increasing stresses until it is completed at the strain ε_M whereupon the stress rises sharply. On unloading the retransformation starts at a lower stress and terminates at σ_{Af}. The value of σ_M-σ_{Af} depends little on the maximum strain $\varepsilon_{\max} \leqslant \varepsilon_M$ reached during the cycle and on the transformation temperature(6). The stress–strain curves are occasionally less regular than shown in the figure, and the exact shape depends somewhat on the crystal orientation(6). When the maximum stress during the cycle is sufficiently high for a different deformation mechanism to start in the transformed martensite(5), the shape of the stress–strain curve during unloading is changed considerably. σ_M depends strongly on temperature; in Fig. 2 is plotted the result for one crystal which has repeatedly been cycled in compression at different temperatures (72 times in total). Cycling was started at 93°C and continued to 130°C, whereupon the temperature was raised again. (The data-points are represented by dots.) A second set of experiments was made after the sample had been left at room temperature for 50 days (points marked by crosses). As is seen all the data points lie on a single straight line with little scatter. An exception are often the first few cycles in a virgin crystal(6) (not shown in the figure). The tensile samples show at similar low scatter in σ_M as long as the stress remains always below the critical stress σ_B at which the "memory type" plastic deformation(5) of the martensite sets in. Although the deformation strain disappears together with the induced martensite on unloading, σ_M is altered in the subsequent cycles. Figure 3 demonstrates this effect: In a first series σ_B (σ_M marked by dots) was never reached, in a second series σ_B (marked by squares) has been reached at least once and σ_M in the cycles that follow is altered (denoted by circles). Before the third series was started the sample was left at room temperature for

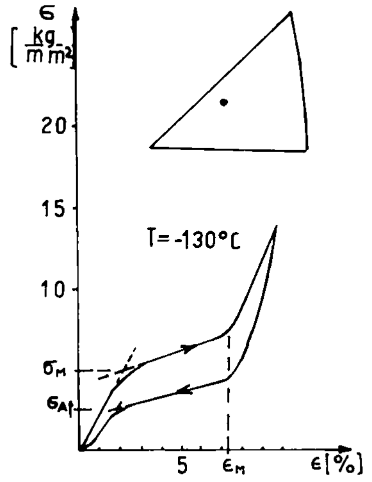

FIG. 1. Stress strain curve during a loading unloading cycle in compression.

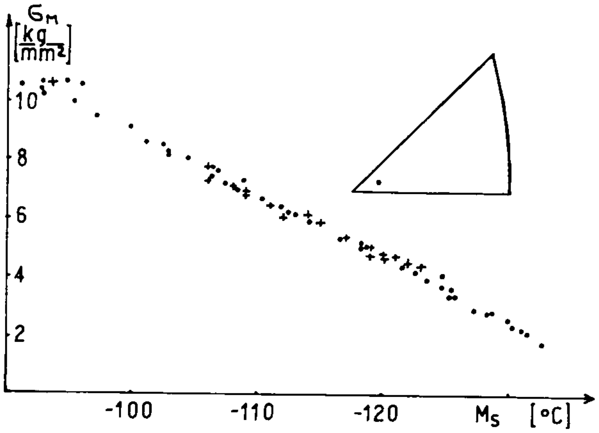

FIG. 2. σ_M as a function of temperature for a sample deformed in compression.

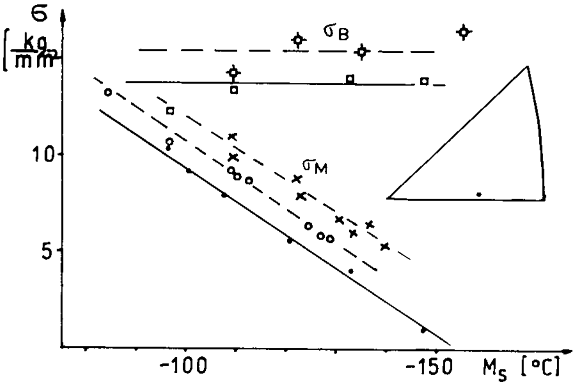

FIG. 3. σ_M and σ_B as a function of temperature for a sample deformed in tension. (σ_B the critical stress for the plastic deformation of the martensitic crystal.)

30 hr. The recovery has a marked influence on σ_M(X) and on σ_B (-┼-). In order to obtain reliable measurements of σ_M it is therefore necessary to remain always below σ_B during the transformation cycles.

By extrapolating the $M_s(\sigma_M)$ curves to zero stress the M_s temperatures for spontaneous martensite are obtained. The results from the compression (○) and tensile samples (□) are plotted in Fig. 4 together with the values for the burst type martensite in polycrystals (X) taken from the paper by Pops and Massalski.(1) The scatter of our values may partially be due to the extrapolation procedure, but it is likely that most of it results from small composition variations of the single crystals. This is corroborated from measurements of M_s by acoustic emission,(6) which show the same trend. The good agreement with the data of Pops and Massalski demonstrates that within experimental scatter M_s is independent of grain size and furthermore that the stress induced martensite corresponds to the burst type martensite. The surface upheavals associated with the formation of stress induced martensite have been studied with the optical stage. The transformation generally manifests itself by the appearance of one predominant set of surface markings. Lines corresponding to other variants are occasionally observed, especially during the beginning of the transformation and at the ends of the samples. It was not possible to distinguish between a "thermoelastic" and a "burst" type martensite, in contrast to the observations in polycrystals in which

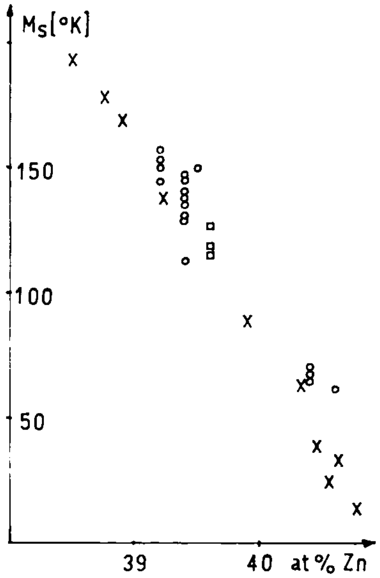

FIG. 4. Extrapolated M_s temperatures vs zinc concentration for compression samples (○), tensile samples (□), and burst type M_s temperatures for polycrystals from (1). (X).

FIG. 5. Surface markings in a partially transformed crystal (bar corresponds to 0.1 mm).

a partially transformed crystal. When the transformation goes to completion the markings disappear again. Upon unloading the traces of the same habit variant become visible again, but no markings remain after the retransformation is completed. This pattern is observed even if the crystal has been stress cycled the "thermoelastic" lines appear at a distinctly higher temperature than the "burst" type bands during a temperature cycle without applied stress.(1) The transformation proceeds by the formation of new bands and by what appears to be a thickening of existing ones. Figure 5 is the photo of a surface from many times. The orientation of the habit planes has been analyzed for seven crystals deformed in compression and for two tensile samples. In the stereographic projection of Fig. 6 are plotted the habit plane normal $\mathbf{p}_1'$ and the direction $\mathbf{d}_1'$ of the martensite shear for one variant as calculated from the theory and the corresponding secondary shear plane $\mathbf{p}_2$ and direction $\mathbf{d}_2$. The unit triangles with the highest shear stress component on the $\mathbf{p}_1'$, $\mathbf{d}_1'$ system are different for tension and compression, they are also marked in the figure. The experimentally determined habit plane normals are plotted in such a way that the orientations of the sample axis lie within the unit triangles. As is seen from Fig. 6 all habit plane normals lie near $\mathbf{p}_1'$, an exception only being a crystal with orientation near (110). In this case many habit variants of comparable amount are induced by the stress. These observations lead to the conclusion that the principal habit variant that is induced by stresses is the one with the highest shear stress component. The shear stress component is $\tau_M = \sigma_M\mu_M$ where μ_M is the Schmid factor. In Fig. 7 are plotted the calculated

$$\frac{d\sigma_M}{dM_s}\mu_M = \frac{d\tau_M}{dM_s}$$

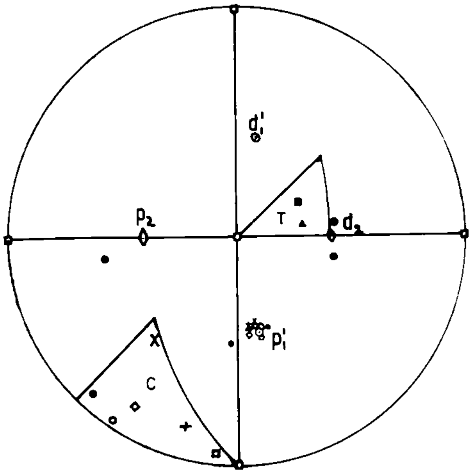

FIG. 6. Stereographic projection showing the calculated habit plane normal p_1' and martensite shear direction $\mathbf{d}_1'$, the secondary shear plane normal $\mathbf{p}_2$ and direction $\mathbf{d}_2$, the unit triangle with the highest shear stress component in tension (in the center denoted by T) and in compression (at the bottom denoted by C). The orientations of the single crystal axes are plotted inside the triangles, and the observed habit plane normals have the same symbols and lie outside the triangles.

for the compression (○) and tension (+) samples as a function of the extrapolated M_s ($\sigma_M = 0$).

In some cases more than one sample was cut from the same single crystal batch, and even in these cases the $d\tau_M/dM_s$ vary from sample to sample. (For example, the highest $d\tau_M/dM_s = 0.139$ kg/mm²K and 0.102 kg/mm²K were obtained for two single crystals of the same batch.) It is likely that the scatter results from the error involved when determining τ_M, especially when ε_M is small. There is no evidence that additional systematic factors contribute to the scatter. From the results of Fig. 7 it is concluded that within experimental scatter $d\tau_M/dM_s$ is independent of crystal orientation and concentration, at least in the range between 39.2 to 40.4 at.% Zn; its value is $d\tau_M/dM_s = 0.096 \pm 0.004$ kg/mm²K.

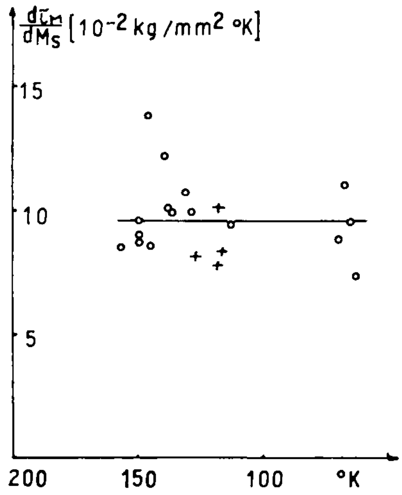

FIG. 7. $d\tau_M/dM_S$ vs M_S for zero stress for compression (○) and tensile samples (+).

It had been shown elsewhere[5] that the "memory type" deformation that starts at a resolved shear stress τ_B in the tensile samples is due to a shear on the plane $\mathbf{p}_2$ in the direction $\mathbf{d}_2$ of the martensitic single crystal: a critical resolved shear stress τ_B of 4.0 ± 0.1 kg/mm² was obtained for the Cu–39.6 at.% Zn alloys. We have now measured τ_B for three tensile samples of 40.4 and 40.6 at.% Zn at liquid nitrogen temperature, the results together with those measured earlier are plotted in Fig. 8. The τ_B apparently depend strongly on the zinc concentration, as is evident from the figure.

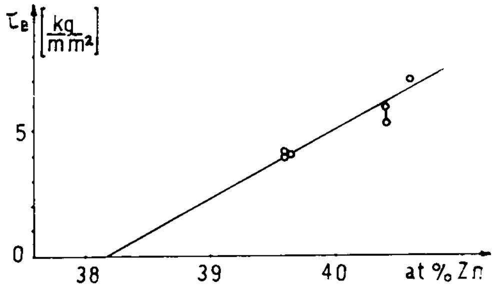

FIG. 8. τ_B as a function of zinc concentration.

DISCUSSION

The temperature T_0 at which the free energy difference between the two phases is zero is expected to lie between M_s and M_{Af}. Since however $M_s - M_{Af}$ is only about 6°C and does not depend sensitively on the temperature[6] little error is introduced by identifying T_0 with M_s. The entropy change then is calculated from $d\tau_M/dM_s$ using the Clausius–Clapeyron equation $\Delta S = \gamma\, d\tau_M/dM_s$ where γ is the amount of martensite shear. γ is obtained from the theory. It depends only little on the Zinc concentration and is $\gamma = 0.17$ for 40.0 at.% Zn. Consequently $\Delta S = (1.63 \pm 0.07).10^{-2}$ kg/mm²K $= 0.31 \pm 0.01$ cal mol K.

It is interesting to compare this value with the entropy difference between the b.c.c. β phase and the f.c.c. α phase, which is stable at lower concentrations. For both phases the Debye temperatures θD have been determined from specific heat measurements near helium temperatures.[7,8] An extrapolation of the θ_D values to 40 at.% Zn give $\theta_D(\beta) = 265 \pm 3$K and $\theta_D(\alpha) = 299 \pm 3$K and for the concentration dependence

$$\frac{d[\theta_D(\alpha) - \theta_D(\beta)]}{dC_{Zn}} = -3.8 \text{ K/at\% Zn}.$$

In the Debye model the entropy S_D at sufficiently high temperatures $T > \theta_D$ is approximately

$$S_D = 3R\left(\frac{4}{3} - \ln\frac{\theta_D}{T}\right). \quad (9)$$

The entropy difference between the α and β phase for the 40 at.% Zn alloy therefore is

$$S_D(\beta) - S_D(\alpha) = 3R \ln \frac{\theta_D(\alpha)}{\theta_D(\beta)} = 0.64 \text{ cal/mol K}.$$

Although it is difficult to assess how $\theta_D(\alpha)/\theta_D(\beta)$ depends on temperature, a smaller entropy change for the martensite transformation is expected since the martensite retains the ordered atom arrangement of the parent β phase. In the concentration range between 39.2 and 40.4 at.% Zn, $S_D(\beta) - S_D(\alpha)$ varies by 13 per cent. A similar possible concentration dependence of ΔS lies within the error limits of the measurements.

As has been discussed elsewhere[5] the critical resolved shear stress τ_B to start the "memory type" deformation of the martensitic single crystals is the stress necessary to move partial dislocations. In the tensile samples the shear system is $+\mathbf{p}_2$, $+\mathbf{d}_2$, i.e. the sign of the shear stress is such that a partial dislocation eliminates stacking faults when it moves. If the stacking falult energy Γ determines the critical shear stress, τ_B is related to Γ by $\tau_B = -\Gamma/b_p$ with $b_p = a(\text{f.c.c.})/\sqrt{6}$ the Burgers vector of the partials. (The minus sign is due to the reduction of the stacking fault area during the movement of a partial dislocation). This implies that the hexagonal phase of the stacking fault is more stable than the face centered phase, i.e. $\Gamma < 0$. A linear extrapolation of the measured τ_B values to zero stress gives a zinc concentration of about 38.2 at.% Zn. If τ_B is determined by Γ, a face centered martensite ($\Gamma > 0$) is expected to be stable below 38.2 at.%. Electron microscopic results have shown that in 37.7 at.% Zn alloys the martensite consists of twinned f.c.c. lamellae,[10] whereas on the basis of X-ray results it had been suggested that the martensite structure in 38.3 at.% Zn is highly faulted[11]. The zinc concentration for which a change in the martensite structure is observed therefore agrees closely with the extrapolated value indicating that τ_B indeed is determined by Γ and that other contributions from athermal stress fields have a negligible influence. Although internal stresses do not contribute to τ_B, a mechanism must exist by which partials are prevented from moving spontaneously into the opposite direction by increasing the stacking fault area (since $\Gamma < 0$). It can be argued that without an applied stress a single moving dislocation has to overcome the stress field of the other partial dislocations on nearby planes, whereas under an applied stress a greater number of partials can move simultaneously without necessarily changing the dislocation configuration, i.e. without a change in the stress fields between nearby dislocations. In Fig. 9 are plotted the Γ values, calculated from $\Gamma_B = -\Gamma/b_p$. A further important consequence of the agreement between the observed and predicted zinc concentration for which $\Gamma = 0$ is that the stacking fault energy is essentially independent of the stacking fault density. This means that to a first approximation the free energy of the martensite can be decomposed into the contributions from a basic structure and from the additional stacking faults.

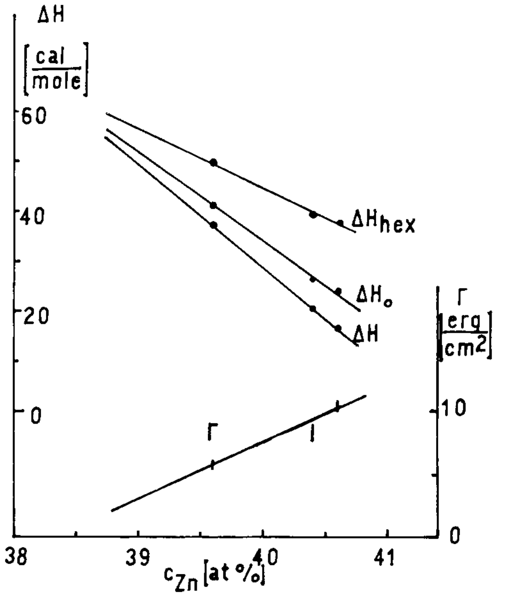

FIG. 9. The concentration dependence of the enthalpy change for the transformation from β-phase to the martensite (ΔH), to the hypothetical *ABCBCACAB* lattice (ΔH_0) and to the hypothetical hexagonal phase (ΔH_{hex}). The lower curve shows the concentration dependence of the stacking fault energy Γ.

Knowing ΔS and assuming that the entropy of a stacking fault is zero, the enthalpy difference ΔH between the β phase and the martensite can be calculated. The results are plotted in Fig. 9 denoted by ΔH. In Fig. 9 are also shown the enthalpy changes for a hypothetical orthorhombic *ABCBCACAB* without faults and for a hexagonal lattice. ΔH and ΔH_0 or ΔH_{hex} are related by

$$\Delta H = \Delta H_0 - (\alpha - \tfrac{1}{3}) \cdot \frac{2\Gamma}{b_{111}}$$
$$= \Delta H_{\text{hex}} + (\tfrac{1}{2} - \alpha)\frac{2\Gamma}{b_{111}}.$$

α is the stacking fault density in a face centered lattice and can be calculated from the theory(12,13), $b_{111} = 2a(\text{f.c.c.})/\sqrt{3}$ is the thickness of a stacking fault.

Figure 9 shows that the slope $\mathrm{d}\Delta H_0/\mathrm{d}c_{\mathrm{Zn}}$ differs little from $\mathrm{d}\Delta H/\mathrm{d}C_{\mathrm{Zn}}$, therefore the variation of the stacking fault density α is not responsible for the strong concentration dependence of M_s. ΔH has also been decomposed into ΔH_{hex} and a stacking fault term. A hexagonal phase is an equilibrium structure in several alloys based on copper around an electron concentration e/a of 1.4–1.5.(14)

As is seen from Fig. 9, ΔH_{hex} and Γ varies with the zinc concentration. As has been discussed elsewhere,(2) the concentration dependence of M_s for binary and ternary alloys based on Cu–Zn is related mainly to c/a and not to the electron concentration e/a, and the tetragonality c/a is due to the order which the martensite inherits from the β-phase. The variation of ΔH_{hex} and of Γ with the zinc concentration therefore has to be correlated to the atomic order, but not or only to a minor degree to the influence of the electron concentration. It is not surprising that the stacking fault energy Γ depends on c/a: Γ represents the energy difference between the hexagonal and the face centered phase whose structures are distinguished by the different stacking order on next nearest planes. Therefore Γ is expected to be sensitively influenced by the interatomic distances. The atomic volume of the martensite is the same as that of the original β-phase within a few per mil and does not change noticeably in the small concentration range under consideration.(15) Thus, changes of interatomic distances are related to variations in the tetragonality c/a, which depends strongly on the zinc concentration. Although the electron concentration does not affect the concentration dependence of ΔH_{hex}, the electronic contribution to ΔH_{hex} most likely is not negligible and has to be taken into account when alloys of a widely differing composition are studied. Only in a sufficiently small concentration range this variation can be neglected, as is the case for the ternary Cu–Zn alloys investigated by Pops and Massalski.(1)

The structure of the martensite that is observed has the orthorhombic stacking *ABCBCACAB*(15) and is not hexagonal, although the hexagonal lattice is the more stable one according to the present discussion. The reason can be sought in the additional requirement that the amount of secondary shear is determined by the condition that an undistorted habit plane exists. Whereas the shears can always be distributed in such a way that a twinned face centered martensite results if this type of structure is sufficiently stable, a hexagonal phase corresponds to a fixed amount of secondary shear, which, except by accident, is different from the amount necessary to obtain an undistorted habit plane. Therefore the hexagonal martensite does not form even if it is the stablest configuration, unless the condition of an undistorted habit is modified. The latter case probably occurs in Au–Cd, where the distortions of the interface are reduced by the formation of a martensite plate in twin orientation in the adjacent region.(16) In this way twinned hexagonal lamellae form which expand as a whole sideways into the matrix with an interface of minimum distortion which can be considered as a second habit plane. In order that this twinned hexagonal martensite be favoured, the stacking fault energy Γ must have a sufficiently high value to compensate for the energy of the twin interfaces.

It has to be emphasized that the present description of the stability of the martensite is only a first approximation: A possible entropy contribution due to the regular arrangement of stacking faults in the orthorhombic *ABCBCACAB* structure has been neglected. Furthermore the stacking fault energy may depend to a minor degree on the distribution and density of the stacking faults, and on the electron concentration. It has been observed indeed that the martensite in Cu–Zn–Ga consists of a mixture of orthorhombic *ABCBCACAB* and of hexagonal *ABAB* lamellae.(15) This may be an indication that such a mixture has a lower energy than a *ABCBCACAB* lattice which contains additional faults.

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