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Probing the ordering transformation in the alloy $Cu_{69}Zn_{14}Al_{17}$ with positrons

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The ordering transformation in the $Cu_{69}Zn_{14}Al_{17}$ shape-memory alloy has been studied with Doppler-broadened annihilation-radiation line-shape-parameter (S) and lifetime measurements. The S-parameter profile as a function of temperature, $S(T)$, from room temperature to 825 K shows $\beta \rightarrow B2$ and $B2 \rightarrow DO3$ transitions in conformity with resistivity measurements. The constancy of the $S(T)$ profile in the heating and cooling cycles is indicative of positrons sampling the equilibrium vacancies. Results obtained from both measurement techniques are not indicative of the presence of divacancies in the disordered (β) state. Analysis of the $S(T)$ profile in terms of a trapping model over the entire temperature range shows a temperature dependence for the vacancy-formation energy, probably due to the ordering process. The results are discussed.

I. INTRODUCTION

The ordering transformation in alloys occurs when a random arrangement of solvent and solute atoms is replaced by a regular or orderly arrangement of different atoms at preferential lattice sites. The alloy Cu-Zn-Al is an important shape-memory alloy and shows two ordering transformations, namely, the disordered β (body-centered cubic) to $B2$ (CsCl-type structure) transition, and the $B2$ to $DO3$ (BiF_3-type structure) transition.[1] The study of a shape-memory alloy requires reproducible and stable transformation temperatures. However, in this alloy the reverse-transformation temperatures A_s and A_f progressively increase with prolonged holding at temperature below M_s subsequent to quenching from above β to the $B2$ ordering transformation.[2] This phenomenon, known as stabilization of martensite, is thought to be caused by the annealing out of the excess vacancy concentration in quenched-in structures.[2] Therefore, it is important to establish the effect of ordering on the vacancy concentration. The equilibrium vacancy concentration, which is a function of the vacancy-formation energy and temperature, is expected to be different for different ordering transformations. In addition, a change in the nature of the vacancies may take place and may be caused by such transformations.

The sensitivity of the positron-annihilation technique to vacancies in metals and alloys is well documented[3] and this technique is most suitable for obtaining qualitative and quantitative information about the equilibrium vacancies associated with the ordering transformation. Order-disorder transformations and vacancy properties have been investigated by means of the positron-annihilation technique in various alloys, e.g., Ni-Al,[4] Cu-Zn,[5] and Cu_3-Au.[6,7] However in Cu-Zn-Al, although several investigations using positrons have been reported,[8–12] the emphasis has been mainly on the nature of the vacancies associated with the martensitic transformation. A systematic investigation of the effect of ordering on vacancies is still lacking. In the present work we report our results on the effect of ordering on certain aspects of the equilibrium vacancies based on positron-annihilation spectroscopy.

II. EXPERIMENTAL

The sample of Cu-Zn-Al alloy was prepared by induction melting of pure Cu, Zn, and Al metals in a graphite crucible. The material was later hot rolled and dissolved in an argon atmosphere at 973 K. Chemical analysis revealed the composition to be 69 at. % Cu, 14 at. % Zn, and 17 at. % Al. X-ray diffraction was used to determine the volume fraction of the α phase in this alloy which was found to be 7% (wt %). Four-probe ac resistivity measurement was carried out as a function of temperature in order to determine the $\beta \rightarrow B2$ and $B2 \rightarrow DO3$ ordering transition temperatures.

^{22}Na was deposited between two identical disks of the sample (8 mm$\phi \times 3$ mm). The assembly was in contact with a thermocouple and was mounted on a furnace. Doppler-broadened annihilation radiations were measured in the temperature range from 825 K to room temperature (cooling cycle) using a 2-cc HPGe (high purity germanium) detector coupled to a 4-K multichannel analyzer (MCA). The detector resolution was <1.1 keV at the 511.8 keV gamma line of ^{106}Ru. In addition, measurements at several points were carried out on a heating cycle encompassing the entire temperature range. The spectrometer was stabilized and $\sim 10^6$ counts were accumulated under the peak for each measurement for which the S parameter, defined as the ratio of counts in the central low-momentum region to that in the entire annihilation peak, was evaluated.

Positron-lifetime measurements were carried out on aged and step-quenched samples, i.e., in one case the alloy was directly quenched in ice-cold water from 973 K (disordered state) and in another case it was quenched in a boiling-water bath and then slowly cooled to room temperature after 1 h. The lifetime spectrometer was a fast-fast coincidence setup with a time resolution of 240 ps. A 10-microcurie source of ^{22}Na deposited on a thin (4-μm) Al foil was sandwiched between the identical sample disks. The response function of the spectrometer was evaluated by carrying out measurements on super pure Al (which provides a single lifetime component 166 ps) and using the code RESOLUTION.[13] This also enabled us to obtain the source contribution. The response function consists of two Gaussians of full width at half maximum (FWHM) 238 ps (85%) and 320 ps (15%) and the source contribution was found to be 450 ps (4.5%). The lifetime spectra were analyzed using the code POSITRONFIT.[13]

III. RESULTS

Resistivity measurements on the Cu-Zn-Al sample show two discontinuities at ~620 and ~790 K (Fig. 1) which, we believe, correspond to the ordering transitions $B2 \rightarrow DO3$ and $\beta \rightarrow B2$, respectively. Figure 2(a) shows that the S parameter increases linearly with temperature from room temperature up to 600 K. However, at ~618 K it responds to a fluctuation [Fig. 2(a)]. From ~645 K onwards, the S parameter increases sharply up to 797 K, beyond which it saturates up to 825 K. A differential of the S parameter is plotted for the entire temperature range in Fig. 2(b) showing two discontinuities corresponding to the temperatures observed in the resistivity measurements. The measured S parameters for the heating and cooling cycles were seen to be the same.

Analysis of the lifetime (τ) spectra of the quenched sample yields a single component after correcting for the source contribution and is seen to be 161±1 ps. On aging there is a marginal decrease in τ, e.g., 157±0.5 ps and 156±0.5 ps at mean aging time of 31 and 56 h, respectively. The step-quenched sample also showed a single component of 135±1 ps.

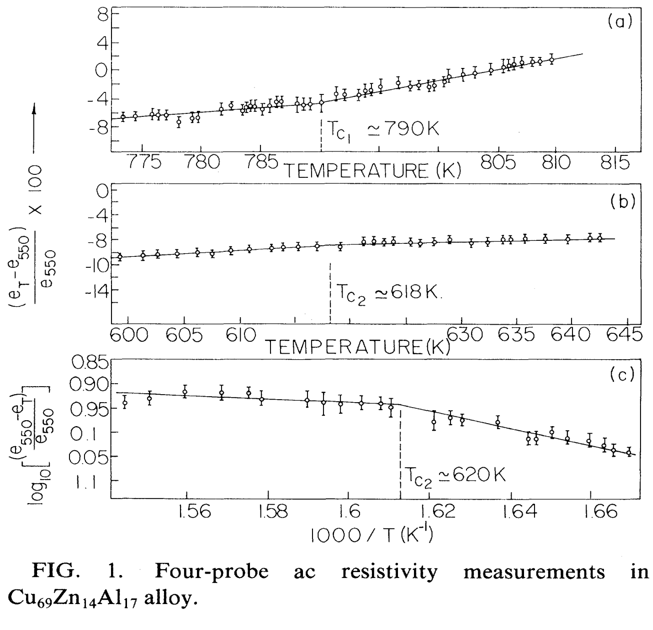

FIG. 1. Four-probe ac resistivity measurements in $Cu_{69}Zn_{14}Al_{17}$ alloy.

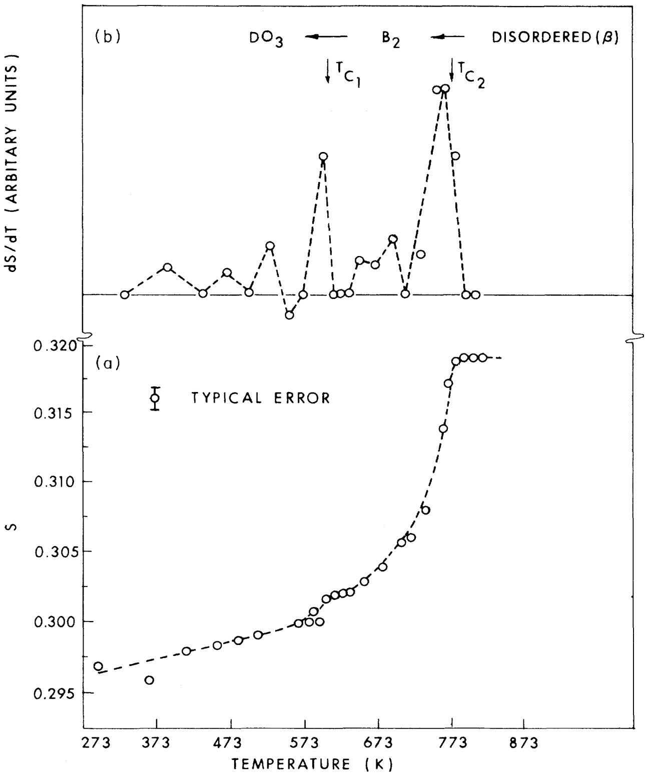

FIG. 2. Temperature dependence of S parameter (a) along with its differential (b) for Cu-Zn-Al shape-memory alloy. Ordering transition temperatures are denoted by T_{c1} and T_{c2}.

IV. DISCUSSION

In order to interpret the data, knowledge on whether positrons interact with the equilibrium thermal vacancies in the alloy is necessary. The reproducibility of the S-parameter profile vs temperature on heating and cooling cycles confirms that the positrons sample the equilibrium thermal vacancies. In the S-parameter profile, the discontinuity at ≈618 K and the subsequent sharp rise reaching a saturation at 797 K are the most interesting observations in the present experiment [Fig. 2(a)]. A differential of the S-parameter profile [Fig. 2(b)] clearly shows two peaks at ≈618 and ≈787 K which correspond to the breaks seen in the resistivity curve at temperature ≈620 and ≈790 K, respectively (Fig. 1). As there are two ordering transitions in this alloy, we believe the observed discontinuities in the S-vs-temperature curve are the result of ordering transitions viz. $\beta \rightarrow B2$ and $B2 \rightarrow DO3$. To confirm these conclusions, the two transition temperatures in Cu-Zn-Al were computed using the Bragg-William-Gorsky formulation and published values of the first- and second-nearest-neighbor interchange energies.[14] The computed temperatures are 799 K for the $\beta \rightarrow B2$ and 638 K for $B2 \rightarrow DO3$ transitions. These values are quite close to the experimental observations.

The β-to-$B2$ transition shows the maximum change in the S parameter compared to the $B2\rightarrow DO3$ transition [Fig. 2(a)]. This is due to the fact that the change in the vacancy concentration associated with the order-disorder transition ($\beta\rightarrow B2$) is much greater compared to that associated with the $B2\rightarrow DO3$ transition. In the disordered state, the saturation of the S parameter indicates a vacancy concentration $>10^{-3}$. The sharp rise in the S parameter in the disordered state indicating formation of divacancies[5] was not seen at least up to 825 K. With ordering, the rapid fall in the vacancy concentration is indicative of a low value of the vacancy-formation energy. With further decrease in the temperature, the equilibrium vacancy concentration is likely to be reduced. Therefore we believe that the fluctuation (at 618 K) associated with the second transition is likely to be affected by the change in the lattice parameters, in addition to the usually expected change in the vacancy concentration. On further lowering of the temperature, the observed linear decrease in S is attributable to the lattice contraction alone.

The positron lifetime is inversely proportional to electron density. In the presence of vacancies, positrons are trapped and experience a less-than-average electron density compared to bulk; consequently there is an increase in the positron lifetime. The single component lifetime of 161 ps for the sample directly quenched from the disordered state reflects the presence of a large concentration of vacancies and does not necessarily indicate the presence of divacancies as reported by Kim and Buyers[5] in β brass. On aging, τ is reduced marginally to 157 and 156 ps for mean aging time of 31 and 56 h, respectively. In contrast, the step-quenched sample which is free from quenched-in defects, gives a single component τ of 135 ps in the martensitic phase similar to the observation made by Plotkowski and Panek.[12]

To arrive at characteristic quantitative details about the vacancies, i.e., vacancy-formation energy associated with the ordering process, the S parameter as a function of temperature, $S(T)$, was fitted using the trapping model.[15] In this model the vacancy concentration is assumed to be controlled by a vacancy-formation energy E_v^f.

$$S(T)=\frac{S_f(1+\alpha T)+S_v(1+\beta T)A_v e^{-E_v^f/kT}}{1+A_v e^{-E_v^f/kT}}\,, \tag{1}$$

where S_f and S_v are the free- and trapped-state contributions to S, α and β are the thermal-expansion coefficients, and k is the Boltzmann's constant and

$$A_v=\mu_v\tau_f e^{(S_{\mathrm{va}}/k)}\,, \tag{2}$$

where μ_v, τ_f, and S_{va} are the positron trapping rate, the free-positron lifetime, and the nonconfigurational entropy of vacancy formation, respectively.

α, β, A_v, and E_v^f were allowed to vary in the fitting procedure, and the initial-guess values were given as $\approx 10^{-5}$/K, 10^{-5}/K, 10^5, and 0.50, respectively. Data from 628 K and above were taken for the fitting and it turned out that the functional form (1) did not yield a good fit (variance of the fit >9.0) when the entire data from room temperature to 825 K were considered. Even in the range of 628–825 K with the four variables mentioned above, a good fit could not be obtained (variance of fit >8.0). Any attempt in fixing α, β, and/or A_v yields a value of ~ 1.0 eV for E_v^f with an equally bad fit with variance ~ 8.0. This variance could be marginally improved to 6.0 on increasing A_v much beyond the reasonable limit (an order of magnitude more) of its value of $\sim 10^5$ in metals and alloys. These observations point to the inaccuracy of the obtained E_v^f values.

If the process of ordering causes a variation of vacancy-formation energy, i.e., an increase in E_v^f with ordering due to variation of configurational entropy with temperature,[5] then it will be difficult to describe the observed S-vs-T profile with Eq. (1). Therefore we introduced a temperature dependence for E_v^f, a factor similar to an order parameter,[5] e.g.,

$$E_v^f=E_v(0)+U(1-T/T_c)^{1/2}\,, \tag{3}$$

where $E_v(0)$ is the vacancy-formation energy in the disordered state, T_c is the ordering temperature, and U is a constant with $U=0$ at $T\geq T_c$. With this consideration we get a reasonably good fit for S between 628 and 825 K with the α and β in the range of $\sim 1.1-3.0\times 10^{-5}$/K, A_v and $E_v^f \sim 4\times 10^5$, and 0.70, respectively. The best fit with a variance of <1.3 was obtained for $U=0.3$ eV. It is seen therefore that the vacancy-formation energy has a temperature dependence, i.e., with ordering E_v^f increases. We kept α/β and A_v as variables in order to have a check on the internal consistency of the fit as these values are known to be in the range of $\sim 1-2\times 10^{-5}$/K and $\approx 10^5$, respectively.

We have seen that the discontinuity in S at ≈ 618 K is a manifestation of the second ordering transition ($B2\rightarrow DO3$); we attempted to fit the complete curve with a functional form incorporating the effect due to both the ordering, namely,

$$S(T)=\frac{S_f(1+\alpha T)+S_{v1}(1+\beta T)A_v e^{-E_{1v}^f/kT}+S_{v2}(1+\beta T)A_v e^{-E_{2v}^f/kT}}{1+A_v e^{-E_{1v}^f/kT}+A_v e^{-E_{2v}^f/kT}}\,, \tag{4}$$

where S_{v1} and S_{v2} are the contributions to the S parameter from the $B2$ phase (just above 618 K) and β phase, respectively, and

$$E_{1v}^f=E_{1v}(0)+U1(1-T/T_{c1})^{1/2}\,, \tag{5}$$

$$E_{2v}^f=E_{2v}(0)+U2(1-T/T_{c2})^{1/2}\,. \tag{6}$$

T_{c1} and T_{c2} are the transition temperatures as measured in this experiment for the $B2\rightarrow DO3$ and $\beta\rightarrow B2$ transitions [Fig. 2(b)] and U_1 and U_2 are constants with $U_1=0$ at $T\geq T_{c1}$ and $U_2=0$ at $T\geq T_{c2}$. E^f_{1v} and E^f_{2v} are the vacancy-formation energies corresponding to the two transitions and $E_{2v}(0)$ is the vacancy-formation energy in the disordered (β) state. Since the ordering ($\beta\rightarrow B2$) is complete at ≈ 628 K, E^f_{2v} was frozen at 628 K or

$$E^f_{2v}(T\leq 628\text{ K})=E^f_{2v}(628\text{ K}) . \tag{7}$$

In addition, it is logical to consider $E_{1v}(0)$ to be the same as E^f_{2v} at 628 K, just above the $B2\rightarrow DO3$ ordering (seen at 618 K). Therefore,

$$\begin{aligned} E_{1v}(0)&=E^f_{2v}(628\text{ K})\\ &=E_{2v}(0)+\{U_2(1-T/T_{c2})^{1/2}\}_{T=628\text{ K}} . \end{aligned} \tag{8}$$

Considering the conditions in Eqs. (7) and (8) and taking α/β and $E_{2v}(0)$ as variables, the data over the entire temperature range were fitted to the functional form (4). U_1 and U_2 were varied between 0.05 and 0.45 and the results obtained are as follows:

A very good fit (variance <1.1) resulting in the values $A_v\approx 3.7-3.9\times 10^5$, $E_{2v}(0)=0.72$ eV, $E_{1v}(0)=0.85$ eV, $\alpha=1.7\times 10^{-5}$/K, and $\beta=2.10\times 10^{-5}$/K with $U_1=U_2=0.3$ eV is obtained. The fitted curve is represented by the dashed line in Fig. 2(a). An attempt to split A_v, i.e, keeping A_{v1} and A_{v2} for T_{c1} and T_{c2}, respectively, yielded the same value, i.e., $A_{v1}=A_{v2}$, indicating that the nature of vacancies is the same throughout, in other words, they were primarily monovacancies even in the disordered state. This corroborates our observations based on lifetime measurements in the quenched samples.

The obtained low value of vacancy-formation energy (0.72 eV) and its temperature dependence explains the sharp rise in the S parameter just before it goes to the disordered state and its subsequent saturation. In addition, the quality of the fit over the entire range of data and the resultant reasonable values of A_v, α/β, and even the vacancy-formation energy shows the consistency of our model on positron trapping based on the assumption of two ordering transitions. However, we feel that the accuracy of the values extracted could be improved with a still higher number of data points.

In conclusion, we have detected the two ordering transformations in the Cu-Zn-Al shape-memory alloy using the positron-annihilation technique. The vacancy-formation energy is seen to be low (0.72 eV) in the disordered state and has a temperature dependence, i.e., it increases with the ordering of the alloy. No evidence of divacancies in the disordered state could be obtained from this experiment.

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