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Phase transition effects of the Mg–Cd system on the positron annihilation parameters

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Abstract: Positron annihilation measurements made on Mg–Cd alloys are considered. Some pronounced effects at the order–disorder transition were found when the alloy composition was close to stoichiometry. No apparent effects of the order–disorder transformation were exhibited when the alloy was far from the stoichiometric composition. The measured mono-vacancy energies of the system at the stoichiometric composition showed a pronounced decrease when the alloy passed from an ordered to a disordered state.

1. Introduction

The sensitivity of the positron to lattice defects, impurities and various other impurity complexes can be further exploited to investigate changes and phase transitions in alloys (Dekhtyar *et al* 1963, Belaidi 1980, Belaidi and West 1982, Belaidi *et al* 1987, Belaidi and West 1988).

The order–disorder transformation often occurs at a particular temperature, called the transition temperature, where thermodynamic quantities like entropy, volume, heat capacity, etc, change discontinuously. A first-order phase transition involves discontinuous changes in volume and entropy whereas a second-order phase transition is described by a discontinuity in heat capacity and in thermal expansion and compression coefficients.

A disordered system tends to either order or precipitate. However, both ordering and precipitation may happen discontinuously within a small range of temperatures. Order–disorder transitions obtained using positron annihilation techniques have been studied by various workers (Dekhtyar *et al* 1963, Moriga 1971) but either small effects (CuAu, Ni₃Mn) or none at all (Cu₃Au) were observed on the angular correlation measurements for the ordered and disordered phases. However, more recent *h* parameter measurements on Cu₃Au, CuZn and Cu–Pd (Doyama *et al* 1974) show significant changes due to order–disorder transitions.

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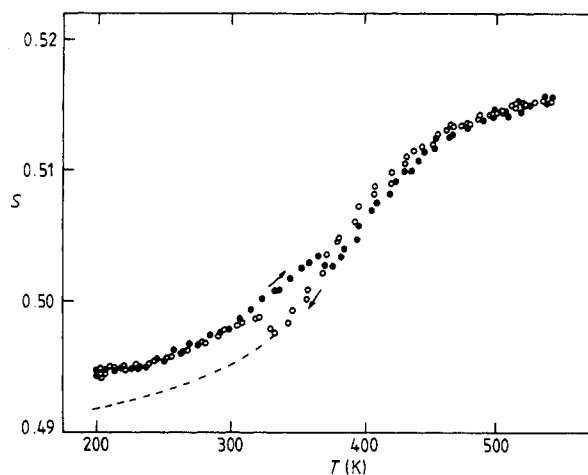


Figure 1. S -parameter against temperature for an MgCd_3 alloy. The order–disorder transition is apparent in both the cooling (\circ) and heating (\bullet) paths of the temperature cycle at 10 K h^{-1} .

Such phase transformations are often associated with already present lattice defects or with defects generated during the transformations. These defects are mainly of the open volume type and therefore can be expected to have a measurable effect on positron behaviour.

2. Results and discussion

The phase diagram of Mg–Cd alloys (Hansen 1958) shows a complete solid state miscibility for temperatures above 526 K. At lower temperatures, the diagram exhibits a region where the alloys undergo order–disorder transformations together with superlattices based on Mg_3Cd , MgCd and MgCd_3 .

Three different alloy samples—Mg–85 at. % Cd, Mg–75 at. % Cd, Mg–70 at. % Cd—and pure Mg and Cd were studied. The Mg–75 at. % Cd alloy is of particular interest, since the ideal compound, MgCd_3 , has a superlattice structure that results from an ordering of the close-packed hexagonal solid solution analogous to the much studied ordering of the face-centred cubic solutions of AuCu_3 . The MgCd_3 compound goes through the order–disorder transformation at 353 K.

The results of an S -parameter measurement on a MgCd_3 alloy are given in figure 1. Following a long anneal (about 24 hours at 550 K) the sample temperature was gradually decreased at a rate of 10 K h^{-1} to 200 K. It was then reheated again at 10 K h^{-1} to the original temperature. In the cooling run the S -parameter shows the usual steady decrease down to 330 K. A clear discontinuity then occurs, presumably because of the phase transformation. Below 330 K the S -parameter continues to decrease, but more slowly. Here, as is clearly shown by the heating run, the change in S is reversible and is probably due to the usual thermal expansion and vibration effects in the ordered system.

The S -parameter of the ordered state lies above the one extrapolated from the disordered state to lower temperatures. The ordering of the MgCd_3 alloy is, however, accompanied by a decrease of about 0.54% in the specific volume, which is, in the main, opposite to that suggested by the increase in the S -parameter. Similar observations have been made by Fukushima and Doyama (1977) on the ordering of Cu–15 at. % Mn and by Hood *et al* (1976) on the α – β transformation of the Zn–47 at. % Ti alloy.

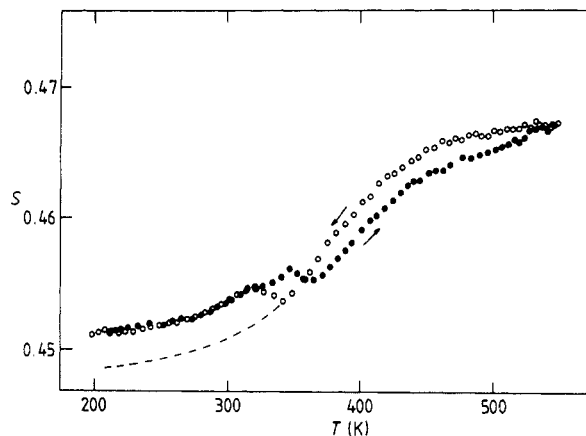


Figure 2. *S*-parameter against temperature for an MgCd_3 alloy at a cycling rate of 5 K h^{-1} . The hysteresis width is reduced at a lower cycling rate.

The transition temperature suggested by the heating curve is at 370 K, as opposed to 330 K in the cooling curve. Above 370 K the heating curve appears to lie slightly below the cooling curve, suggesting some memory effect.

It is often suggested that the stresses generated by a phase transformation can result in the formation of lattice defects. Defects play an important role in atomic diffusion processes and are often an important factor in allowing transitions to take place. Thus an interpretation of the present results in terms of such non-equilibrium defects is tempting. Such interpretations have been offered by Fukushima and Doyama (1976) to explain effects in angular correlation of the order–disorder transformation in AuCu and by Nagai *et al* (1976) in regard to GP zone formation studies in Al–Cu and Al–Cu–Sn alloys. However, in neither of these cases was a complete cooling and heating cycle studied. In the case of the present results the influence of a transient non-equilibrium defect population is made implausible by the reversibility and reproducibility of the low temperature ($T < 330 \text{ K}$) part of the curve. The ‘memory’ effect above 370 K previously noted may suggest that an appreciable part of the low temperature ordered phase persists even in the highest temperature region. Thus the lower values of the *S* parameter in the heating curve suggest a reduced positron trapping effect that might be associated with either a modified positron trapping rate σ_{1V} or a different value of E_{1V} .

To investigate further the influence of the temperature cycling rate on the hysteresis effects exhibited in figure 1, a run was made on the same sample but at half the cycling rate (5 K h^{-1}). The result of this measurement is shown in figure 2, and exhibits a convergence of both forward and reverse transition temperatures towards the ‘true’ transition temperature of the MgCd_3 alloy. Hysteresis effects of this nature have been observed in x-ray diffraction patterns on MgCd_3 alloys (Edwards *et al* 1952) and can be taken as a characteristic of a first-order phase transition. They also suggest that the transformation does not occur at the point where the free energies of the two phases are exactly equal but that some supercooling and some superheating is always necessary for the transformation to take place (Rao and Rao 1978, 1966). By taking an average of the forward and reverse transformation temperatures found above we obtain an order–disorder transition temperature of about 348 K. This value corresponds rather well with previous estimates made from electrical resistance determination by Grube and Schiedt (1930) and from a determination of specific heat, in which a peak was found at 350 K (Khomyakov *et al* 1950).

Table 1. The apparent formation energies for the Mg–Cd system.

Specimen	T_c (K)	E_{1V} (eV) by T_c method	E_{1V} (eV) by Arrhenius plot	E_{1V} (eV) from other works
Cd	377 ± 4	0.455 ± 0.005	0.50 ± 0.01	0.44 ^a 0.45 ^b 0.45 ^c 0.52 ^d
Mg-85 at.% Cd	331 ± 4	0.399 ± 0.005	0.37 ± 0.01	—
Mg-75 at.% Cd				—
1. Ordered			0.40 ± 0.1	
2. Disordered	282 ± 4	0.340 ± 0.005	0.34 ± 0.01	
Mg-70 at.% Cd	322 ± 3	0.388 ± 0.004	0.38 ± 0.01	—

^a Hood and McKee (1978).

^b Mackenzie and Lichtenberger (1976).

^c Fellows (1979).

^d Seeger (1973).

Primed superscript: results from curve fitting. Non-primed superscript: results from T_c method.

Another effect of the decreased cycling rate is the larger difference between the heating and cooling curves in the 400–500 K temperature range (figure 2). However, recalling our previous suggestion of residual effect of the ordered state we would assert that the approximate doubling of the time spent by the alloy in the low temperature region even more strongly ‘freezes in’ the ordered state. Again, the direction of the change in figure 2 suggests decreased positron trapping.

Both the Mg–85 at.% Cd and Mg–70 at.% Cd alloys are well off stoichiometry and thus are expected to behave differently from the compound $MgCd_3$, which has a stoichiometric composition.

Indeed, no effect of ordering was observed in these alloys. Similar results were obtained by Kuribayashi *et al* (1975), who found no anomalous change in their angular correlation measurements on Cu–10 at.% Pd at the order–disorder transition and by Fukushima and Doyama (1977) who observed no precipitation effect in Cu–2.3 at.% Ag.

Table 1 shows significant effects of alloying on the apparent formation energy of a monovacancy in a binary alloy. As can be seen, a strong apparent decrease in E_{1V} occurs when the alloy is close to stoichiometry. These results agree with the angular correlation measurements by Fukushima and Doyama (1977) on Cu–Mn alloys. Their results also show a reduced value of E_{1V} for the disordered state of Cu–15 at.% Mn (Cu_5Mn). The effect of order–disorder transition on the atomic mobility was also reported by Kuper *et al* (1956) in diffusion coefficient measurements on Cu, Zn and Sb in β -brass. A clear increase was observed in the activation energy for self-diffusion as the alloy went from a disordered to an ordered state. If we assume that the apparent formation energy of a monovacancy is about half this activation energy, a smaller value of E_{1V} is suggested for the disordered state.

This difference between the vacancy formation and related activation energies in ordered and disordered states of an alloy may be explained in the following way. In an ordered alloy the atoms of each component have definite positions with respect to the atoms of the other components and are arranged in such a way as to minimise the free

energy of the system. Any atomic diffusion that occurs in this ordered state will disrupt this atomic order and thus increase the free energy of the system relatively more than in an alloy where there is already some disorder.

3. Conclusion

In the Mg–Cd system the positron shows the well established sensitivity to equilibrium defects (West 1979) and sensitivities to the solid–solid phase transformations.

The interpretation of the underlying phenomena is, however, somewhat different from that offered in previous reports of the positron studies of order–disorder transitions, a result we attribute to certain inadequacies in the earlier works.

The vacancy formation energy deduced for the cadmium was consistent with the values obtained in other works. The measured monovacancy energies of the system in the stoichiometric Mg₃Cd alloy showed a pronounced decrease when the latter passed from an ordered to a disordered state. This result which again is similar to that obtained in other works (Fukushima and Doyama 1977, Kuper *et al* 1956) is explained in terms of the effect of ordering upon atomic diffusion.

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