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Positron annihilation in solid, liquid and undercooled melts of $Co_{80}Pd_{20}$

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Abstract. Positron annihilation measurements have been performed in solid, liquid and undercooled $Co_{80}Pd_{20}$ alloy using electromagnetic levitation as containerless processing method. The formation enthalpy for a single vacancy is $H_{1v} = (1.7 \pm 0.1)$ eV. In the melt, the thermal expansion continues linear in the undercooled phase and is larger than that of the solid alloy. The mean free volume in the liquid phase is slightly larger than the volume of a single vacancy. At the Curie temperatures of both solid and liquid phase, the S-parameter indicates no effect on the atomic structure. Different H_2 concentrations in the processing gas atmosphere have no detectable influence on the data.

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In recent experiments it has been shown that molten CoPd alloys, especially the composition $Co_{80}Pd_{20}$, can be undercooled below the Curie temperature of the solid phase $T_c(s)$. Electromagnetic levitation is used in order to avoid heterogeneous nucleation induced by container-walls [1], so undercooling up to 340 K is possible. Evidence has been found for the existence of long-range magnetic ordering in the undercooled liquid phase [2]. From measurements of the magnetic susceptibility, the Curie temperature of the undercooled melt could be extrapolated to $T_c(l) = 1253\,K \pm 8\,K$ [3]. Hence, a magnetic state was found in a fully relaxed system in contrast to, for example, amorphous ferromagnets. At this point the interesting question arises whether the atomic structure is changing in the undercooled melt near the magnetic phase transition. Several experimental techniques are available for the study of atomic structures, e.g., X-ray diffraction or EXAFS (Extended X-ray Absorption Fine Structure). Some preliminary experiments using EXAFS at DESY Hamburg were performed [4]. However, up to now, these measurements are not sufficiently precise to prove a possible change of the atomic structure in the liquid state since the Debye–Waller factor of the melt causes a high attenuation of the signals. New measurements with further improvements are in preparation.

The present experiments were performed using positron annihilation as an indirect method to study changes of the atomic configuration. It has been shown that this method is capable to detect, e.g., transitions from a hexagonally close-packed (hcp) to a face-centered cubic (fcc) lattice in Co [5] or the transitions between a body-centered cubic (bcc) and fcc lattice structures in Fe [6]. Measurements in Ni show a decreasing Doppler broadening of the 511 keV annihilation line with increasing temperature in solid as well as in liquid and in undercooled Ni. However, measurements in the melt were reported only in a narrow temperature range up to 140 K below the melting point [7]. In [8, 9] data from the undercooled melt are reported up to 300 K undercooling, however, with rather poor statistics. Many other positron annihilation experiments in liquid metals are reported in literature [10, 11, 12], but our special attention is directed on the undercooled regime.

Experiments on CoPd alloys are facilitated by the presence of ^{58}Co which serves as an internal positron source. After being thermalized within a few ps the positrons are diffusing in the material. Their typical diffusion length is about 100 nm before becoming trapped. Positrons annihilate with electrons of the conduction band or with electrons of the ionic cores into two 511 keV gamma rays. While the transversal momentum of the annihilating electrons causes a slight angular deviation from the 180° emission of the gamma rays, their longitudinal moments cause a Doppler shift. The much smaller momentum of the thermalized positron may be neglected. Thus, the angular correlation and the Doppler broadening of the 511 keV annihilation line contains information on the annihilating electrons. Since the positron lifetime depends on the local electron density, we obtain information on the trapping sites of the positrons.

Any observable physical quantity F of a positron annihilation experiment will take a mean value weighted by the probability P for annihilation in a free or in one or more different trapped states. If we have only free positrons migrating in the lattice and others trapped in vacancies we obtain

$$F = F_f P_f + F_v P_v,$$

where F_f and F_v are the characteristic values of F in the free state and trapped in a vacancy, respectively. Analogously, P_f and P_v are the probabilities to annihilate in the free state or in a vacancy, respectively [13].

For the solid phase, the concentration C_{1V} of single vacancies in thermal equilibrium is given by

$$C_{1v} = \exp(-G_{1v}/kT) \qquad (1)$$

[14], where G_{1v} denotes the Gibbs free energy of single vacancy formation

$$G_{1v} = H_{1v} - TS_{1v}. \qquad (2)$$

H_{1v} denotes the formation enthalpy and S_{1v} the formation entropy of a single vacancy, k is the Boltzmann constant and T the temperature.

If μ is the capture rate per vacancy and λ_f the annihilation rate in the free state, the concentration of single vacancies is given by the ratio [13]

$$C_{1v} = ((F - F_f)/(F_v - F))^* \lambda_f/\mu \qquad (3)$$

or

$$(F - F_f)/(F_v - F) = (\mu/\lambda_f)^* \exp(S_{1v}/k)\exp(-H_{1v}/kT). \qquad (4)$$

By fitting equation (4) to the measured temperature dependence of positron annihilation the formation enthalpy H_{1v} of a single vacancy can be determined.

1 Specimen preparation and experimental procedure

^{58}Co was used as an internal positron source. Commercial $^{58}CoCl_2$ was solved into buffered alcalic solution (the same method as for the quantitative Co analysis [15]). A 10 μm Pd foil was used as cathode, a Pd wire served as anode. At 3.5 V, an activity of 10 – 20 μCi of ^{58}Co was electroplated onto the Pd foil. This foil was pressed into a slit of $Co_{80}Pd_{20}$ sphere of 6 mm diameter and a purity better than 99.99%. In the RF levitation apparatus, the foil was molten into the sample. During melting in an He (80%) H_2 (20%) atmosphere at normal pressure less than 3% activity was lost.

High-purity environmental conditions were established in an electromagnetic levitation apparatus to process the sample in a containerless state. The sample was placed in a quartz tube surrounded by a water-cooled Cu coil which carried a radio frequency (260 kHz) current of maximum power of 5 kW. The temperature was measured contactlessly by a two-colour pyrometer ($\lambda_1 = 950$ nm, $\lambda_2 = 1050$ nm) with an absolute accuracy of ± 5 K. It was calibrated at the liquidus temperature $T_l = 1606$ K, which was independently determined by differential thermal analysis measurements [16]. Before starting the experiment the quartz tube was evacuated and then refilled with a gas mixture consisting of 80% He and 20% H_2 providing a continuous cooling stream through the tube. H_2 was added in order to reduce solid oxides on the surface of the sample which otherwise may cause heterogeneous nucleation. This reduction became more efficient by strongly overheating the sample before cooling down. It proved that about 2 minutes of overheating at 2000 K led to a reasonable undercooling. The temperature of the sample was controlled by a proportional-integral-differential (PID) circuit combined with an electromagnetic valve governing the gas stream and thus the heat transfer from the sample to the surrounding gas. This experimental setup allows measurements in solid as well as in liquid material. Undercooling up to 340 K below T_l was achieved, sometimes for a duration of more than one hour. Once an undercooled sample crystallized, data recording was stopped within one second. The data of different runs could be added to each other.

The integral Doppler shift, the Doppler broadening of the 511 keV line, was measured with a Ge-detector (1.8 keV FWHM and 35.3% efficiency). In order to get a high accuracy, it is important that the resolution of the detector does not change with time. The stability of the electronics was permanently checked by analysing the 811 keV line of ^{58}Co. In order to preserve the energy resolution of the Ge detector independently of RF power, the detector and the electronics were carefully shielded and grounded.

The analysis of data was performed by introducing the lineshape parameters S and W. S is obtained as the number of counts in a certain central part of the 511 keV annihilation line divided by the integral counts of the complete line. Complementary W denotes the counts outside the central part of the annihilation line divided by the counts in the whole line. Thus, W is especially sensitive to annihilation events with high electron momentum, as e.g. in ion cores, which contribute to a large Doppler broadening, while S is more representative for annihilation in vacancies or free volume. For each data point about $2 \cdot 10^6$ events in the 511 keV line were measured.

2 Results

Figure 1 presents the temperature dependence of the S-parameter for solid (□) and for liquid (●) $Co_{80}Pd_{20}$.

In the solid state the S-parameter increases slowly with a slope of $9.64 \cdot 10^{-6}$/K up to about 1000 K which indicates a volume extension due to thermal expansion of the crystal. In this temperature range we may attribute the annihilation to freely diffusing, i.e. untrapped positrons in the crystal. Above 1000 K the S-parameter increases much stronger due to trapping of positrons in thermal vacancies. The dashed line indicates a saturation of the S-parameter above 1000 K once the solidus temperature $T_s = 1561$ K is reached, i.e. all positrons are trapped by a high concentration of thermal vacancies.

For temperatures within the region of coexistence of liquid and solid phase (■), the S-parameter continues to increase, due to an increasing contribution from positrons annihilating in the liquid phase which shows throughout a larger S-parameter than the solid. The data of the liquid phase yield a linear increase of the S-parameter with a slope of $1.25 \cdot 10^{-5}$/K, which continues linearly into the undercooled regime.

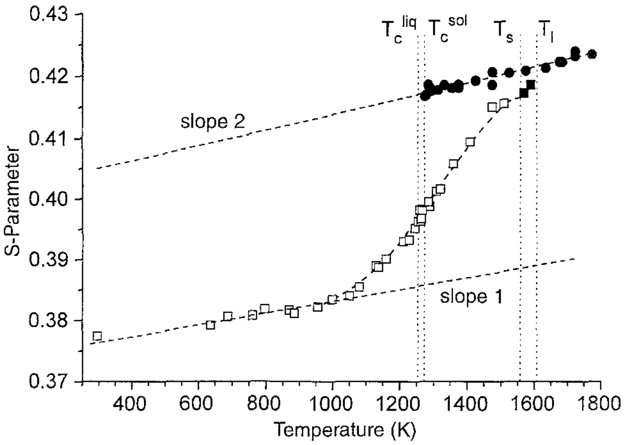

Fig. 1. Temperature dependence of the S-parameter in solid (□) and in liquid (●) $Co_{80}Pd_{20}$. The pronounced increase of the S-parameter in the solid between 1000 K and the solidus temperature $T_s = 1561$ K is due to annihilation of positrons trapped in an increasing concentration of thermal vacancies. Between T_s and the liquidus temperature $T_l = 1606$ K solid and liquid phase coexist (■) and S increases due to a higher content of the liquid phase for which S is significantly higher. Near the Curie temperatures of the solid and liquid phase $T_c(s) = 1271$ K and $T_c(l) = 1253$ K no effect on S is detectable. The error is within the symbol size

Neither in the solid nor in the liquid phase any effects on the S-parameter were detectable as the Curie temperatures were crossed or approached.

In the temperature range between 1000 K and T_s the activation enthalpy for the formation of a single vacancy in solid $Co_{80}Pd_{20}$ could be determined as $H_{1v} = (1.7 \pm 0.1)$ eV. To this end an Arrhenius plot of $\ln((S(T) - S_f(T))/(S_v - S(T)))$ was used. The temperature dependence of the S-parameter for the free state $S_f(T)$ was taken into account by extrapolating the straight line (slope 1) in Fig. 1 up to T_s. S_v denotes the S-parameter for positrons annihilating in vacancies in the case of saturation.

Figure 2 gives an enlarged plot of data at temperatures above 1200 K. Additional data are included which were obtained in different atmospheres to investigate any influence of H_2 on the short range structure. (□) represent the data for solid, (■) the data in the coexistence regime of solid and liquid, and (●) for liquid $Co_{80}Pd_{20}$ processed with an He(80%) H_2(20%) atmosphere. (▲) represent the data processed in He(97%) H_2(3%) and (▼) in pure He. No difference is observed between data obtained in different He/H_2 atmospheres.

3 Discussion

For the present experiments electromagnetic levitation was preferred to a crucible technique for two reasons. Firstly, heterogeneous crystallization on container walls during large undercooling had to be excluded, and secondly, an unknown disturbing background of positrons annihilating in the material of the crucible had to be avoided. These advantages carry the penalty of a less precise pyrometric temperature measurement. Using a two colour pyrometer an accuracy of ± 5 K was achieved, which is less precise than measurements with thermocouples in contact with a crucible.

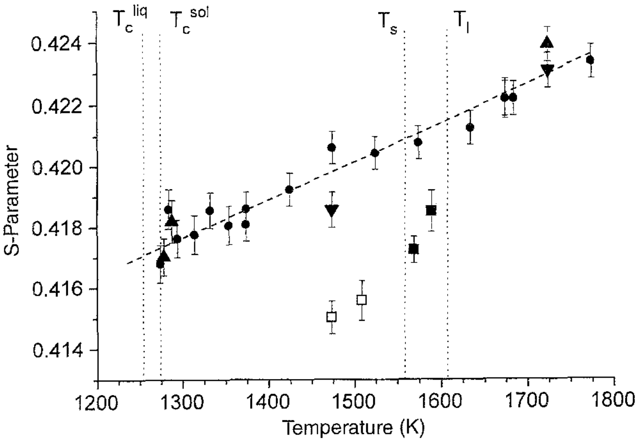

Fig. 2. Plot of the data of Fig. 1 above 1200 K. Data obtained from the liquid phase in atmospheres of different compositions are distinguished. (□) represent the data for solid, (■) the data in the coexistence regime of solid and liquid, and (●) for liquid $Co_{80}Pd_{20}$ processed with an He (80%) H_2 (20%) atmosphere. (▲) represent the data processed in He (97%) H_2 (3%) and (▼) in pure He

Approaching the solidus temperature $T_s = 1561$ K the S-parameter becomes saturated and its value may be attributed to annihilation of positrons trapped in vacancies. Therefore, we may use this value as a calibration point for positron annihilation in a single vacancy volume, i.e. an atomic volume corrected for relaxation effects.

The temperature dependence of the S-parameter gives us the activation enthalpy of vacancy formation $H_{1v} = (1.7 \pm 0.1)$ eV. This value falls in the range between the respective values for the pure metals $H_{1v}(Co) = (1.34 \pm 0.07)$ eV [5] and $H_{1v}(Pd) = (1.85 \pm 0.25)$ eV [17]. This seems reasonable because the alloy is not chemically ordered.

The S-parameter in the liquid phase is in saturation, i.e., all positrons are trapped in free volume. The small increase with slope 2 in Fig. 1 may be explained by thermal expansion of the free volume analogously to the thermal expansion of the solid phase, which causes an increase of the S-parameter for positrons in the free state in the lattice (slope 1). Slope 2 is about 25% larger than slope 1, which indicates that the thermal expansion in the liquid phase is larger than for the solid.

The somewhat larger S-parameter measured for the liquid phase indicates that the probability of annihilation of trapped positrons with core electrons of high momentum is decreased. Thus we conclude that the mean free volume in which the positrons annihilate must be slightly larger than the volume of a single vacancy. However, an influence of a trapped positron on the free volume is not detectable with this method.

Assuming that the same trapping rate for the solid state holds also in the liquid, we may roughly estimate from the saturation of the S-parameter in the liquid phase a concentration of the free volume of at least 10^{-4}.

Between T_s and T_l the S-parameter increases, although the S-parameters of both the solid and liquid phase are in saturation. This may easily be explained by an increasing fraction of liquid phase with significantly larger S-parameter in the region of coexistence.

No effect is apparent close to the Curie temperature $T_c(l) = 1253$ K of the liquid as well as that of the solid $T_c(s) = 1271$ K by means of positron annihilation, whereas other methods as, e.g., measurements of the paramagnetic susceptibility of muon spin rotation show clear magnetic effects [2,3,18]. For pure Co, self-diffusion measurements also do not show any significant effect at the magnetic phase transition [19], whereas in diffusion data on α-Fe a magnetic transformation is clearly visible [20]. By means of positron annihilation in α-Fe, also no magnetic effect could be detected [6]. $T_c(s)$ in iron is far below the temperature where thermal vacancies have influence on the S-parameter. We conclude that there is no significant change of free volume caused by a transformation of the atomic structure in the melt close to $T_c(l)$.

The W-parameter is sensitive to the annihilation in ion cores, where the electrons have a higher momentum than that of the conduction band. Regarding the W-parameter, a similar gap between liquid and solid phase is observed. This indicates that the annihilation in the free volume is similar to the annihilation in a thermal vacancy and affirms that the mean free volume exists of holes, which are slightly larger than one atomic volume.

Since the solubility of H_2 is unknown for the liquid alloy, we tested the influence of varying H_2-concentrations on the positron annihilation.

As shown in Fig. 2 no significant changes could be observed. This indicates a low solubility of H_2 and hence no effect on atomic distances which would be important for the magnetic behaviour.

4 Conclusions

Positron annihilation measurements have been performed in solid, liquid and undercooled state. By using a containerless electromagnetic levitation technique and pyrometric temperature measurement the specimen could be kept in an undercooled state for several hours at temperatures up to 340 K below the liquidus temperature. This allowed annihilation measurements with small statistical errors. The S-parameter was measured and served as an indirect parameter for changes of the atomic structure. No changes could be detected near the Curie temperature of both the solid and the liquid phase. From the temperature dependence of the S-parameter the activation enthalpy of single vacancy formation could be obtained as $H_{1v} = (1.7 \pm 0.1)$ eV. A slight linear increase of the S-parameter with increasing temperature in the liquid and in the solid phase (below the detectable onset of vacancy formation) shows a similar thermal expansion of the lattice and the structure of the liquid. No difference of thermal expansion in the undercooled melt and in the liquid above T_l was observed. The mean free volume in the liquid phase turned out to be slightly larger than the volume of a single vacancy in the solid.

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