Appl. Phys. 20, 135–140 (1979)

Applied Physics

Phase Transformations and Vacancy Formation Energies of Transition Metals by Positron Annihilation

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Received 28 May 1979/Accepted 2 July 1979

Abstract. The technique of the coincidence count rate at the peak of the angular correlation curve (CCR) in positron annihilation has been applied to the investigation of vacancy formation energies in thermal equilibrium in nickel, cobalt, and iron. The monovacancy formation energy E_{1v}^F has been determined to (1.55 ± 0.05) eV and (1.34 ± 0.07) eV for nickel and cobalt, and (1.60 ± 0.10) eV for α-iron, and (1.40 ± 0.15) eV for γ-iron, respectively. The structural phase transformations in cobalt (693 K) and iron (1183 K, 1663 K) are exhibited by discontinuities of the CCR. In the case of cobalt the CCR follows exactly the change of the thermal expansion at the transition temperature. The temperature dependence of the CCR in the prevacancy region is found to be proportional to the thermal expansion for all metals investigated.

PACS: 78.70, 71.60, 61.70

Positron annihilation has been proved to be a very sensitive and powerful tool for the determination of defects in metals, cf. [1,2]. Measuring the positron lifetime, Doppler broadening or the coincidence counting rate at the peak of the angular correlation curve (abbreviated hereafter as CCR) as a function of temperature and analyzing the data in terms of the trapping model [3–5] yields accurate values for the formation energy of monovacancies E_{1v}^F [2]. When extending the experiments to a temperature range above 1300 K, difficulties may arise in the case of Doppler broadening and lifetime measurements if "sandwich"-type or similar arrangements of samples and positron source are used. Source material diffusing into the sample might be a very serious effect. Thus, the CCR technique seems to be better suited for high-temperature experiments since external sources can be used. In this paper CCR measurements on Ni, Co, and Fe are presented and the corresponding values of E_{1v}^F are determined. Attention is paid to the influence of phase transitions on the CCR. Besides magnetic transitions in all these metals (cf. Table 1) both cobalt and iron show structural phase transformations. In cobalt the structure changes from hcp to fcc at 693 K. Pure iron transforms from a bcc (α-iron)- to a fcc (γ-iron)-phase at 1183 K and back to a bcc-structure at 1663 K. All metals investigated have melting points around 1800 K.

As described previously [2], the temperature dependent CCR is given by

$$F(T) = F_f\left(1 - \frac{\mu c_v \tau_f}{1 + \mu c_v \tau_f}\right) + F_v \frac{\mu c_v \tau_f}{1 + \mu c_v \tau_f}, \tag{1}$$

$$F_f = F_0\left(1 + \beta \frac{\Delta l}{l}\right), \tag{2}$$

$$c_v = \exp\left(\frac{S_{1v}^F}{k}\right) \exp\left(\frac{-E_{1v}^F}{kT}\right). \tag{3}$$

F_f and F_v is the counting rate expected if all positrons are "free" in the lattice or trapped at vacancies, respectively; μ is the positron trapping constant, and

0340-3793/79/0020/0135/$01.20

Table 1. Temperatures of the magnetic transitions and of the structural phase transformations in nickel, cobalt, and iron

Metal	Magnetic transition T_C[K]	Structural transformation T[K]
Ni	618	None (fcc)
Co	1388	693 (hcp→fcc)
Fe	1043	1183 (bcc→fcc) 1663 (fcc→bcc)

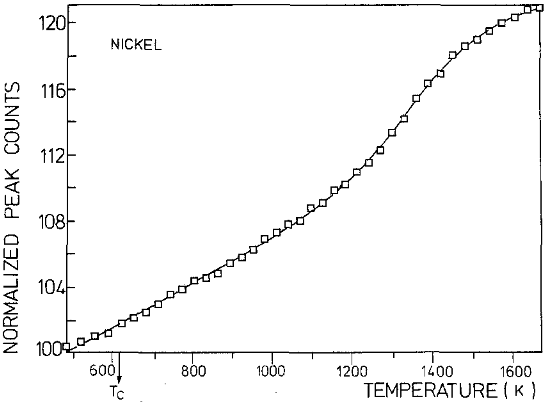

Fig. 1. Coincidence counts at the peak of the angular correlation curve after correction for source decay and background as a function of temperature, for nickel. The temperature T_C of the magnetic transformation is indicated. The statistical standard deviation is within the size of the symbols used. The solid line represents the best fit of (1)

τ_f the lifetime of the positrons in the "free" state. In (2) F_0 is the counting rate at 273 K, where trapping is negligibly small. β is a constant determined from the experimental data and $\Delta l/l$ is the linear thermal expansion. The monovacancy concentration c_v is given by two exponential functions involving E^F_{1v} as well as the formation entropy for monovacancies S^F_{1v}. Using a computer program the parameters F_v, F_f, $\mu e(S^F_{1v}/k)$, and E^F_{1v} were determined by fitting (1) to the data points. The values for τ_f and $\Delta l/l$ are taken from [6, 7, 14].

1. Experimental Procedure

The isotope ^{64}Cu was used as a source for the positrons. Thin foils of high-purity copper were irradiated for about 24 h in the Merlin reactor (Kernforschungsanlage Jülich) at a flux of approx. 10^{14} neutrons/cm^2 s. The intensity of the source was about 800 mCi.

The source was placed into a collimator system so that no positrons could annihilate at the walls of the UHV-sample chamber seen by the two detectors. The source holder and the sample chamber were cooled by water. Through a lock mechanism a source could be replaced every 24 h, a time corresponding roughly to about two half lives of ^{64}Cu.

The samples were cylindrical (8 mm dia., 15 mm high) with a spherical shaped top surface. They were heated in a tantalum resistance furnace, isolated from the furnace by ThO$_2$ ceramics. The temperature was controlled and measured by a W/Re-thermocouple inside the sample. The nominal purity of Ni, Co, and Fe was 99.999%. Previous to the measurement the samples were annealed for several hours close to their melting points in a purified argon atmosphere of 1.2×10^5 Pa and then very slowly cooled down to ambient temperature. All measurements were performed in a high-purity argon atmosphere. The whole temperature range was cycled several times with a measuring time of 1000 s per temperature point. The angular correlation apparatus used was of the type of a conventional long-slit geometry with lead slits in front of the 60 cm long NaI-detectors. The geometrical resolution was 2 mrad. Corrections of the CCR due to small changes of sample shape as well as for the motion of the sample towards the source as the sample expands with increasing temperature were made by the single counting rates. The contribution of background was subtracted from the measured CCR. The windows of the discriminator of each detector were set for the photopeak of the 511-keV annihilation irradiation only in order to exclude the Compton scattered events in the sample.

2. Results and Discussion

2.1 Nickel

The experimental CCR of Ni versus temperature in the temperature range from 470 to 1710 K is shown in Fig. 1.

Up to 970 K there is an almost linear increase of the CCR as a function of temperature, whereas above 970 K a more than linear increase is observed due to vacancy trapping, tending to saturation close to the melting point. This typical behavior of the CCR has been observed already for various metals [2].

The increase of the CCR below 970 K is proportional to the thermal expansion of nickel, the factor β in (2) being 7.1. The solid line in Fig. 1 shows the result of the fit to the data points, using values for $\Delta l/l$ from [6] and $\tau_f = 1.73 \times 10^{-10}$ s [7]. A value of (1.55 ± 0.05) eV is obtained for the monovacancy formation energy of nickel. The fitting procedure results in a $\chi^2 = 1.29$ and realistic errors for the parameters used. This shows that the two state trapping model is appropriate for analyzing the data. Within the error limits, this result for E^F_{1v} is in agreement with the values of recent quenching experiments, yielding

$E^F_{1v} = (1.58 - 1.63) \pm 0.05$ eV [8].

However, there is a discrepancy with the results of a positron Doppler broadening experiment of Campbell et al. [9]. From a fit of their data applying the trapping model as well, they obtain $E^F_{1v}=1.73$ eV for nickel with a very small statistical error and a quite large χ^2 of 2.10. Their conclusion, that the trapping model is inappropriate in the case of nickel is not supported by our investigations.

Within the experimental error no discontinuity of the CCR at the Curie temperature $T_C=618$ K is observed. The type of experiments described here is not likely to show changes in the CCR due to purely magnetic effects. For this kind of investigations polarized positrons and homogeneously magnetized samples would be necessary.

Recent measurements [10] of the thermal expansion of Ni around T_C show an increase in $\Delta l/l$ from 0.495 to 0.537% within a temperature interval of 5 K between the ferromagnetic and the paramagnetic state. The overall change of this increase is so small, however, that it cannot be resolved in our experiment in spite of good statistical accuracy (2×10^{-3} standard deviations).

Since the magnetic transformation occurs at a temperature where vacancy trapping is not yet observed, no conclusion about possible changes of the vacancy formation energy in the ferro- and paramagnetic state can be drawn.

2.2 Cobalt

Figure 2 (lower part) shows the CCR for Co. The overall behavior of the curve is similar to that of Ni. After an almost linear increase with increasing temperature in the low-temperature region the trapping effect starts around 1020 K. There is no clear saturation behavior close to the melting point.

In contrast to Ni, however, the CCR of Co shows a discontinuity at its hcp→fcc-transformation (see insert in Fig. 2 with enlarged vertical scale).

These data were obtained after the sample had been annealed for more than 24 h at about 650 K, to achieve a nearly complete hcp structure in cobalt. After annealing, the sample was cooled to room temperature and the data points presented in the insert were obtained going across the transition from low temperature to high temperature. This procedure was necessary because of the complex nature of this phase transformation. The transition from the fcc to the hcp phase (decreasing temperature) is very slow and depends on the grain sizes of the sample, whereas the hcp→fcc-transition occurs almost instantaneously [11, 12]. This behavior results in an inhomogeneous structure of the sample due to the mixed phases when the temperature is cycled; in this case the effect of the phase transition is smeared out. The full curve through the data points in the insert of Fig. 2 is the result of a fit of (2) using the measured values of $\Delta l/l$ [6] and leaving β as a parameter. Within the experimental error, the same β of 3.1 fits the data in the hcp and fcc phase.

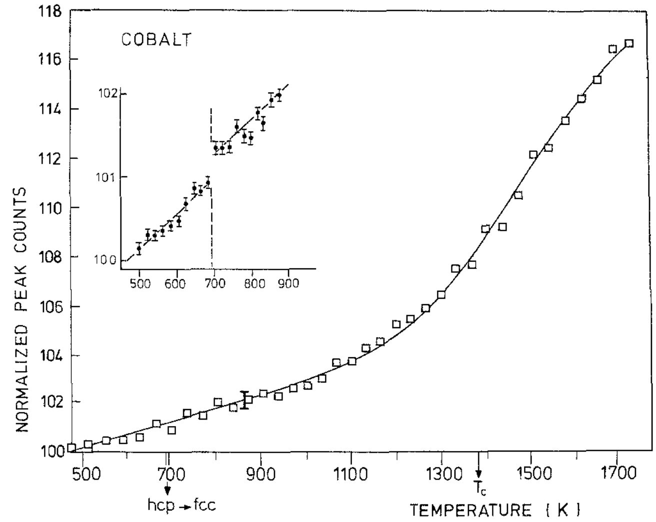

Fig. 2. Coincidence counts at the peak of the angular correlation curve after correction for source decay and background as a function of temperature, for cobalt. The structural and magnetic transformation and a typical statistical error are indicated. The solid line represents the best fit of (1). The insert shows the data of a measurement across the structural transformation (see text). The solid line represents a fit of (2)

This good agreement of β in the two phases is another evidence that at temperatures where trapping of positrons at vacancies is not yet important, the increase of CCR with temperature is proportional to the thermal expansion.

The full line through the data points in the lower part of Fig. 2 is a fit of (1) using τ_f and $\Delta l/l$ from [6, 7]. The χ^2 for the fit is 1.60. The values for $\Delta l/l$ of the fcc-phase have been extrapolated to low temperatures. This is justified because of the relatively fast cooling rate in the temperature cycling, leading to an almost complete fcc structure for cobalt, even at low temperatures. The monovacancy formation energy obtained for cobalt is $E^F_{1v}=(1.34\pm0.07)$ eV. The comparatively large error is due to the fact, that the saturation value F_v of vacancy trapping at high temperatures is not well defined by the experimental data. Although the magnetic transformation ($T_C=1388$ K) occurs at a temperature where vacancy trapping is pronounced, no change of the CCR of cobalt is observed at the Curie temperature within the statistical error. This leads to the conclusion, that the magnetic structure of cobalt does not influence significantly the vacancy formation process in thermal equilibrium.

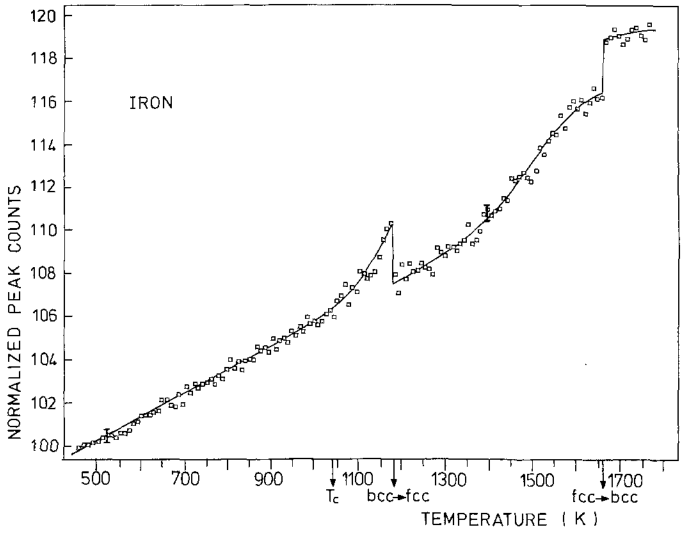

Fig. 3. Coincidence counts at the peak of the angular correlation curve after correction for source decay and background, as a function of temperature, for iron. The magnetic transition and the structural phase transformations are indicated. A typical error bar is indicated for both phases

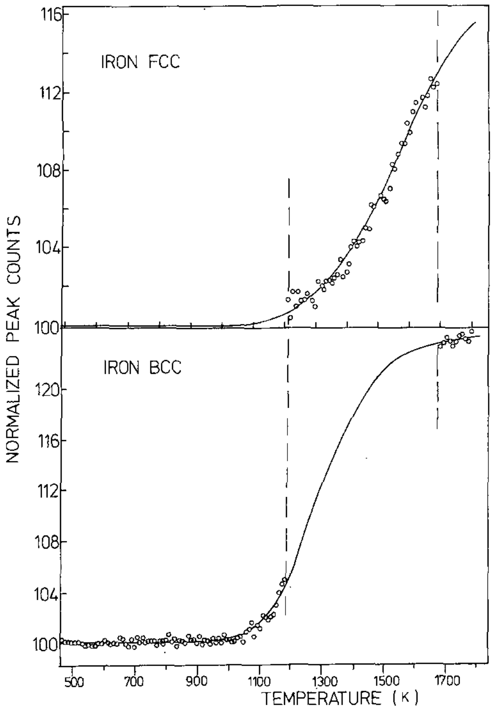

Fig. 4. Coincidence counts at the peak of the angular correlation curve, after correction for source decay, background, and thermal expansion, as a function of temperature, for fcc and bcc iron. The solid lines represent the best fit of (1) to the data in the two phases

2.3 Iron

Figure 3 shows the CCR for pure iron. From 470 K up to approximately 970 K there is again an almost linear increase of the CCR with increasing temperature. Above this temperature the vacancy trapping effect leads to a stronger increase of the CCR. At the bcc→fcc-transformation ($T = 1183$ K) a sharp discontinuity is observed. The CCR decreases by about 15% compared to the total trapping effect and increases again continuously with increasing temperature in the fcc structure up to the phase transition at 1663 K (fcc→bcc), where another discontinuity is found. Above 1663 K (bcc-phase) the CCR tends to saturate. The data can be regarded as consisting of two independent CCR-curves, i.e., one for bcc iron (from low temperatures up to 1183 K and from 1662 up to the melting point) and another for fcc iron in the temperature interval from 1183 to 1663 K (Fig. 4). For bcc iron a subtraction of the thermal expansion effect ($\beta = 6.6$) from the CCR can easily be performed (Fig. 4, lower part), also the saturation value of trapping is well defined by the experiment. The situation for fcc iron (Fig. 4, upper part) is not as good, because there are no experimental data available in the low- and high-temperature region. An analysis of the data on the basis of the trapping model was performed independently for the two phases. The values obtained are $E^F_{1v} = (1.60 + 0.10)$ eV and $\mu\tau_f \exp(S^F_{1v}/k) = (2 \pm 1) \times 10^6$ for bcc iron and $E^F_{1v} = (1.40 \pm 0.15)$ eV and $\mu\tau_f \exp(S^F_{1v}/k) = (4 \pm 2) \times 10^4$ for fcc iron, respectively. It should be emphasized, that the fitting procedure suffers from the lack of data in important temperature ranges for both phases. Therefore the values for the formation energy contain a relatively large error, especially for fcc iron, since F_f and F_v of (1) are not determined by the experimental data. Nevertheless in the fcc phase there is a significantly lower value for E^F_{1v} and the value for $\mu\tau_f \exp(S^F_{1v}/k)$ is about 50 times smaller compared to bcc iron.

Recent calculations of the monovacancy formation entropy in α-iron (bcc) yield a value of $S^{F(\mathrm{bcc})}_{1v} = 2.1k$ [13]. Substituting $\tau^{(\mathrm{bcc})}_f = 1.10 \times 10^{-10}$ s [14] and the calculated S^F_{1v} into $\mu\tau_f \exp(S^F_{1v}/k)$ for α-iron, we obtain $\mu^{(\mathrm{bcc})} = (2.2 \pm 1.1) \times 10^{15}\ \mathrm{s}^{-1}$ for the positron trapping constant. Using $E^{F(\mathrm{bcc})}_{1v} = 1.6$ eV and $S^F_{1v} = 2.1k$, a vacancy concentration of $c_v = 2.8 \times 10^{-4}$ is obtained at the melting point.

The CCR curve for iron reported here is in good agreement with the data of Schaefer et al. [15], obtained in a Doppler broadening experiment. Our evaluation, however, indicates that also in iron thermal expansion alone allows a very good description of the results in the temperature range between 450 and 950 K and that there is no necessity for introducing self-trapping and also no evidence for it [16, 17]. As in the cases of Ni and Co, no change of the CCR at the Curie temperature T_C of 1043 K is detected. Since T_C is in a range, where trapping of positrons is just observed, no conclusion about a possible change of E^F_{1v} in the ferro- and paramagnetic state can be drawn from these experiments. Table 1 shows the magnetic transitions as well as the structural transformations of the metals investigated. The values of E^F_{1v} are summarized in Table 2. Columns 4 and 5 of this table contain the self-diffusion energies Q_{SD} and the monovacancy migration energies E^M_{1v} obtained through the relation $Q_{SD} = E^F_{1v} + E^M_{1v}$.

Table 2. Values of the monovacancy formation energy E^F_{1v}, compared with values published by other authors; the selfdiffusion energy Q_{SD} and the monovacancy migration energy E^M_{1v} for nickel, cobalt, and iron

Metal	E^F_{1v}[eV]	Previous E^F_{1v}[eV]	Q_{SD}[eV]	E^M_{1v}[eV]
Ni	1.55 ± 0.05	$(1.58-1.63) \pm 0.05$ [8] 1.73 [9] 1.45 [9]	2.88 [27, 28]	1.3
Co	1.34 ± 0.07		2.94 [29]	1.6
α-Fe	1.60 ± 0.10	1.53 ± 0.15 [15]	2.88[a] [30] 2.45[b] [30]	0.85
γ-Fe	1.40 ± 0.15	1.54 ± 0.15 [15] 1.55 ± 0.06 [25] 1.83 ± 0.14 [25]	2.95 [31]	1.55

[a] Ferromagnetic.

[b] Paramagnetic.

2.4 The Prevacancy Region and Phase Transformations

The temperature region which precedes the temperature where trapping of positrons is observed (prevacancy region) has recently gained much interest. There are different opinions about the origin of the increase of CCR and the respective parameters of Doppler broadening spectra with increasing temperature. In some cases an increase of the parameters at very low temperatures has been observed [18], an effect which might be due to the localization of the positron at gain boundaries. In a region of intermediate temperature, some metals (Cd, In) show an increase of the annihilation parameters [19, 20], which has been analyzed in terms of the self-trapping model [16, 17]. We want to emphasize the importance of thermal expansion for the temperature dependence of the annihilation parameters. The data in the prevacancy region of all experiments presented in this paper can be very well described by a fit of (2), i.e., an effect proportional to thermal expansion. The factor β, (2), depends on the sample material and the definition of the parameter used for evaluation. In our measurements with a fixed experimental set up and the same evaluation procedure we observed that β varies between a value of about three in the case of cobalt (a value which has been observed for other metals as well [2, 9, 21, 22]) and about six to seven for nickel and iron. By alloying iron with small amounts of titanium and vanadium, a decrease of the slope is observed, which is about proportional to the amount of impurities in the sample [23] and is approaching $\beta = 3$ for a concentration of one percent. Another strong evidence that thermal expansion is the dominant effect in the prevacancy region is the behaviour of the CCR at the phase transformations. In the case of cobalt, the CCR follows exactly the discontinuity of thermal expansion at the hcp→fcc-transition (693 K) and the same value of β allows the description of the CCR in both phases. This is not surprising, since the hcp and the fcc phase are structures with the closest packing of the atoms, and the symmetry of an interstitial site is identical in both phases. In this aspect cobalt is a very ideal case, because the consequence of the phase transformation is only a small expansion of the lattice whereas the local atomic symmetry at the interstitial site is maintained. Also experiments on uranium [24] which exhibits structural phase transformations at 941 and 1048 K show that in the prevacancy region the CCR follows the discontinuities of the thermal expansion at the transition temperatures. If, however, there exists a change in the local structure of an interstitial position due to a phase transition, and/or the transformation occurs in a temperature region where positron trapping is important, the different positron annihilation parameters (F_0, F_v, μ, τ_f) as well as the thermodynamical parameters S^F_{1v}, E^F_{1v} have to be evaluated separately as it was done in the case of iron. The fact, that the CCR of cobalt is directly proportional to the change in the thermal expansion at the structural transformation implies that a careful investigation of phase transition phenomena with respect to the positron annihilation parameters might also lead to a better understanding and possibly allow to clarify the origin of the prevacancy effect.

Acknowledgement. We would like to acknowledge the financial support of part of this work by the "Bundesministerium für Forschung und Technologie".

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