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LETTER TO THE EDITOR

Vacancy formation energy in iron by positron annihilation

S M Kim and W J L Buyers

Atomic Energy of Canada Limited, Chalk River, Ontario, Canada KOJ 1J0

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Abstract. The temperature dependence of the positron annihilation peak coincidence rate has been measured in iron from 20°C to 1320°C. The peak rate did not change across the ferro-para magnetic transition at $\sim 770^\circ\text{C}$ but decreased by 1.5% across the α - γ phase transition at 910°C . The trapping model analysis of the data yields values of the vacancy formation energies (E_f) of 1.4 ± 0.1 eV in α -Fe and 1.7 ± 0.2 eV in γ -Fe. The correlation between E_f and T_t , where T_t is the threshold temperature, has been derived from the trapping model.

For a clear understanding of metallurgical properties, in particular the radiation damage and recovery process, it is essential to know the formation and migration energies of point defects. During the last several years the positron annihilation technique has been shown to be useful in studying vacancies, dislocations and voids in metals (West 1973). In particular, thermal equilibrium measurements of the positron annihilation momentum distribution in aluminium (McKee *et al* 1972, Kim *et al* 1974) and several other metals (McKee *et al* 1972, Triftshauser and McGervey 1975) have successfully been applied to obtain the vacancy formation energy. The accuracy of these values is limited by hidden background effects such as the thermal expansion of the lattice and possible positron self-trapping, that is various aspects of the positron-phonon interaction (Lichtenberger *et al* 1975, Kim and Buyers 1976). The transition metals are of particular interest because of their technological importance, and iron was chosen for study because of its widespread use and because no reliable measurements of its vacancy formation energy have been possible with other techniques (see e.g. Seeger *et al* 1970, Franklin 1972).

In this Letter we report accurate measurements of the vacancy formation energy in iron obtained by the equilibrium positron annihilation technique. The long slit (93×1 mrad) peak coincidence method (Kim *et al* 1974) was used with the angular correlation apparatus described previously (Kim and Buyers 1972). The peak coincidence rate was normalised to the singles count rate in the photopeak of one detector in order to correct for the decay of the ^{64}Cu positron source. The high purity (99.99%) iron specimen from the Materials Research Corporation contained small concentrations of oxygen (110 PPM), nitrogen (12 PPM) and carbon (10 PPM). The specimen was a strip of cross section 0.64 cm by 0.16 cm and 10 cm long. A 3.6 cm horizontal section was irradiated by positrons and the ends of the strip were bent to form two vertical 3.2 cm lugs welded to thick steel rods. The rods were electrically connected at a cool point to the copper conductors from the power supply unit for self-heating of the specimen. Prior to the measurements, the specimen was chemically

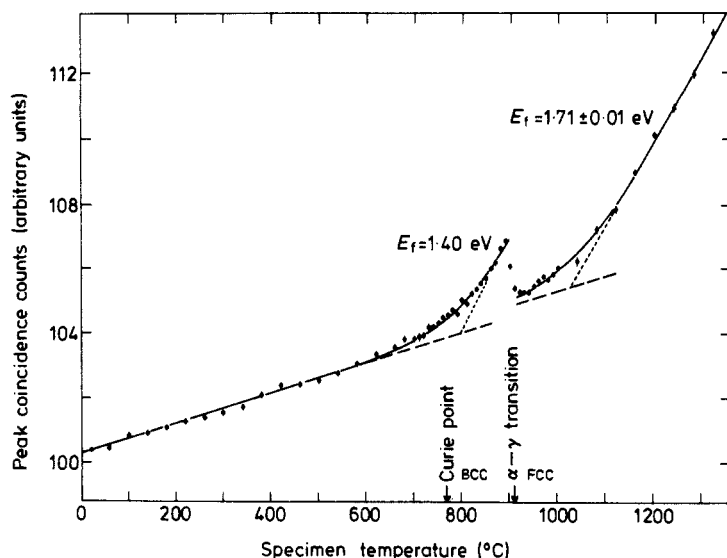


Figure 1. The positron annihilation peak coincidence counts as a function of temperature in Fe (●). The full curves are theoretical fits to the data as explained in the text. Broken lines describe the effect of thermal expansion and the dotted lines the slope of the S curve near the inflection point in both α - and γ -Fe.

etched and annealed for three hours at 860°C. The temperature in °C was measured to $\pm 1\%$ with W5%Re-W26%Re thermocouples welded directly to the sample and was controlled to within $\pm 2^\circ\text{C}$ using the Thermac Series 6000 Control Unit.

The peak coincidence rate was measured as a function of temperature from 20°C to 1320°C. Vacuum runs ($\leq 2 \times 10^{-4}$ Pa at 20°C) were made up to 1000°C. Runs between 920°C and 1320°C were made in an 10 kPa atmosphere of high-purity helium gas so as to reduce sample sublimation. The coincidence count rates were corrected for dead-time effects by extrapolating 20°C data before and after high-temperature measurements. Successive vacuum runs were normalised at 20°C. Successive helium runs were normalised to those obtained in vacuum in the temperature region of overlap, i.e. 920°C to 1000°C.

The temperature dependence of the peak coincidence rate in iron is shown in figure 1. About 6×10^5 to 1.1×10^6 coincident counts were accumulated in 7 to 12 scans at each temperature for the set of runs made below 1000°C, and about 6×10^5 counts in 7 scans for the runs between 920°C and 1320°C. In α -Fe the peak rate increases almost linearly with temperature from 20°C to about 650°C with a slope equal to $4.7 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. This slope is likely to be due to the volume thermal expansion of the lattice ($4.5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$). Above 650°C the peak rate increases exponentially with temperature up to 890°C indicating positron trapping at thermal vacancies in α -Fe. No apparent change of the peak rate can be detected across the ferro-para magnetic transition temperature of $\sim 770^\circ\text{C}$ (*Metals Handbook* 1961). Self-diffusion measurements in α -Fe have shown some evidence that the activation energy of self-diffusion changes from 2.63 eV in ferromagnetic iron to 2.49 eV in paramagnetic iron (James and Leak 1966). If this change is caused entirely by the decrease in the vacancy formation energy, the vacancy concentration would increase by more than 400% at temperatures above $\sim 770^\circ\text{C}$. Our present data, however, show that

a change in the vacancy concentration across the Curie temperature by more than 35% is unlikely, implying a change in the formation energy of less than 1%.

When the temperature is raised above the α - γ (BCC to FCC) phase transformation temperature of 910°C, the peak rate decreases by 1.5%. This decrease is most likely caused by decreased vacancy concentration in the FCC phase since the slope of the peak rate curve just above 920°C is much smaller than that just below 890°C. The atomic volume decreases by 1.2% at the α - γ transition (Pearson 1967), which by itself would suggest a decrease in the free positron coincidence rate, but the fact that the structure also changes results in a net increase as shown by the trapping model analysis described below. The analysis shows that the peak rate for free positrons increases by $0.3 \pm 0.1\%$ at the α - γ phase transition. This result implies that the trapped positron contribution to the peak rate decreases by $1.8 \pm 0.1\%$ at about 910°C. The change in the peak rate across the α - γ phase transition exhibited no appreciable hysteresis.

Above 920°C the peak rate again increases slowly at first and then rapidly with temperature up to 1320°C, indicating positron trapping at thermally generated vacancies in γ -Fe. Above 1320°C accurate measurements of the peak rate could not be made because the specimen tended to deform, possibly as a result of evaporation and softening. Since the γ - δ (FCC to BCC) phase transformation occurs at $\sim 1390^\circ\text{C}$ (Metals Handbook 1961), saturation of the peak rate in γ -Fe cannot be observed even if accurate measurements are made above 1320°C.

The observed temperature dependence of the peak rate was fitted by the trapping model in order to determine the vacancy formation energy E_f in α - and γ -Fe. In this model the temperature dependence of the peak rate is given by (e.g. Kim *et al* 1974)

$$F(T) = \frac{F_f(1 + \alpha T) + F_v(1 + \beta T)A \exp(-E_f/kT)}{1 + A \exp(-E_f/kT)} \quad (1)$$

where F_f and F_v are the free and trapped peak rate respectively, α and β are constants describing the effect of thermal expansion and $A = \mu\tau_f \exp(S/k)$ where μ is the trapping rate, τ_f is the free positron lifetime and S is the entropy of vacancy formation. Since the complete S-shaped curve of $F(T)$ could not be obtained for either α - or γ -Fe, it was necessary to impose certain constraints on one of the parameters of equation (1). A least squares fit with all five parameters ($\beta = 0$ or $\beta = \alpha$ assumed) did in fact converge in α -Fe, but gave unacceptable values of the parameters F_v/F_f and/or A . We fixed the parameter A to lie within the range 5×10^4 to 1.5×10^6 since the majority of the positron measurements of A lie within this range (table 1). In addition, a theoretical estimate by Hodges (1970) gives $A \simeq 10^5$ in aluminium. When the data are fitted with this constraint, we obtain $E_f = 1.4 \pm 0.1$ eV in α -Fe. The formation energy is rather insensitive to the choice of the trapping rate parameter A , and varies only from 1.31 to 1.50 eV over the whole range (30:1) of possible A values. The value of E_f was not sensitive to variations in the thermal expansion parameter for traps, β , i.e. nearly the same value of E_f was obtained for both $\beta = 0$ and $\beta = \alpha$. The fit ($\chi = 0.92$) that gave $E_f = 1.40$ eV was obtained with $A = 3 \times 10^5$ and is shown with a full curve in figure 1. The other parameters being $\alpha = 4.7 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, $\beta = 0$ and $F_v/F_f = 1.152 \pm 0.002$. The value of E_f in α -Fe is in good agreement with the value ~ 1.5 eV obtained indirectly by subtracting the vacancy migration energy 1.1 eV (Glasser and Wever 1969) from the activation energy of self-diffusion 2.6 eV (James and Leak 1966).

Table 1. Experimental values of the parameter $A = \mu\tau_i \exp(S/k)$ and associated E_f for several metals. In some cases A was calculated from the given values of $\mu\exp(S/k)$ using τ_i from the paper by MacKenzie *et al* (1975).

Element	A	$E_f(\text{eV})$	References
Al	2.0×10^5	0.66 ± 0.04	McKee <i>et al</i> (1972)
	$(2.1 \pm 1.1) \times 10^5$	0.67 ± 0.03	Kim <i>et al</i> (1974)
	$(9.9 \pm 0.5) \times 10^4$	0.66 ± 0.01	Triftshauser (1975)
Cd	2.3×10^4	0.39 ± 0.04	McKee <i>et al</i> (1972)
Pb	1.3×10^5	0.50 ± 0.03	McKee <i>et al</i> (1972)
	$(3.3 \pm 0.6) \times 10^6$	0.54 ± 0.02	Triftshauser (1975)
In	3.0×10^7	0.55 ± 0.02	McKee <i>et al</i> (1972)
	$(3.0 \pm 0.6) \times 10^6$	0.48 ± 0.01	Triftshauser (1975)
Zn	4.1×10^5	0.54 ± 0.02	McKee <i>et al</i> (1972)
Cu	4.4×10^4	0.98 ± 0.02	McGervey and Triftshauser (1973)
	$(1.6 \pm 0.4) \times 10^6$	1.29 ± 0.02	Triftshauser and McGervey (1975)
	7.8×10^5	1.21 ± 0.02	Fukushima and Doyama (1976)
Ag	1.7×10^5	0.99 ± 0.06	McGervey and Triftshauser (1973)
	$(2.1 \pm 0.4) \times 10^6$	1.16 ± 0.02	Triftshauser and McGervey (1975)
Au	$(1.3 \pm 0.2) \times 10^5$	0.97 ± 0.01	Triftshauser and McGervey (1975)
	7.0×10^4	0.92	Herlach <i>et al</i> (1977)

The peak coincidence rate data in γ -Fe were also analysed by the least squares method with the same constraints on the parameter A . Since in the γ -phase the effect on the positron annihilation of the thermal expansion cannot be determined from the positron experiment, we have allowed α to vary between 0 and $7.2 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$, the upper limit being set at the volume expansion coefficient in γ -Fe. Within these limits the vacancy formation energy in γ -Fe was determined to be $1.7 \pm 0.2 \text{ eV}$. The lower limit of E_f was obtained with $A = 5 \times 10^4$ and $\alpha = 0$, and the higher limit with $A = 1.5 \times 10^6$ and $\alpha = 7.2 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. The formation energy was not sensitive to variations in β as was also found in α -Fe. The fit ($\chi = 0.92$) that gave $E_f = 1.71 \pm 0.01 \text{ eV}$ was obtained with $A = 3 \times 10^5$ (as in the α -phase) and is shown in figure 1 with a full curve. The other parameters are $\alpha = 4.7 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$, $\beta = 0$ and $F_v/F_f = 1.130 \pm 0.005$. Since the activation energy of self-diffusion in γ -Fe is 2.8 eV (Graham and Tomlin 1963), E_f in γ -Fe is expected to be a little higher than that in α -Fe, in agreement with the present results.

We have also determined E_f in the α - and γ -Fe from the empirical formula obtained by MacKenzie and Lichtenberger (1976). These authors defined the threshold temperature T_i in kelvins by the intersection of the slope of $F(T)$ near the inflection point with the extension of the low-temperature thermal expansion line. They plotted T_i against the known activation energy of self-diffusion, Q , and found a linear relationship, $Q \simeq 28 kT_i$, in many metals. Since $Q \simeq 2E_f$ for most metals, the above relationship implies $E_f \simeq 14 kT_i$. The correlation between E_f and T_i is derived from the trapping model in the Appendix. When this empirical formula is

used we obtain $E_f = 1.3$ eV in α -Fe and $E_f = 1.6$ eV in γ -Fe. Although uncertainties exist in obtaining the threshold temperature of 800°C (α -phase) and 1030°C (γ -phase), they result in very small errors in E_f . These values are in good agreement with those obtained from the trapping model analysis.

Doppler lineshape measurements for iron have recently appeared (Schaefer *et al* 1977), from which vacancy formation energies of 1.53 ± 0.15 eV and 1.54 ± 0.15 eV have been derived for the α - and γ -phases. An earlier analysis of this data, given in figure 2 of Maier *et al* (1977), gave ~ 1.26 eV for the α -phase. The data in the α -phase are interpreted in terms of an S-shaped self-trapping curve (our data are linear in T), and no vacancy induced rise is observed until $\sim 780^\circ\text{C}$ (we observe a rise at 650°C). It is possible that we are more sensitive to the initial rise caused by vacancies because we have more data points in the region of interest, each being the average over many runs. Their formation energies derived for the α - and γ -phases are similar because they have taken the trapping parameter A for the γ -phase vacancies to be ten times smaller than for α -phase vacancies. We do not understand the physical basis for this assumption, and prefer the argument that, since the change in volume per atom at the phase transition is small, the trapping parameters should be of the same order of magnitude in the two phases. We emphasise that it is hazardous to ascribe any physical significance to an E_f and A determined *simultaneously* in a phase such as γ -Fe where saturation has been reached at neither end point.

We wish to thank G M Hood for useful discussions and D C Tennant for expert technical assistance. We are grateful to K Maier of Stuttgart for communicating the preliminary results of Doppler work on iron while this work was in progress.

Appendix. Correlation between E_f and T_i

In deriving the relationship between E_f and T_i from the trapping model of equation (1), we will first consider the case $\alpha = \beta = 0$. If we expand $F(T)$ in a Taylor's series near the inflection point of the S-curve determined by $T = T_0$, where $A \exp(-E_f/kT_0) = 1$, and retain only the linear term in $(T - T_0)$, we obtain

$$F(T) = \frac{F_f + F_v}{2} - \frac{(F_v - F_f) \ln A}{4} + \frac{(F_v - F_f)(\ln A)^2}{4E_f} kT. \quad (\text{A1})$$

Since T_i is determined by the intersection of $F(T)$ with F_f , we have

$$E_f = \frac{(\ln A)^2}{\ln A - 2} kT_i. \quad (\text{A2})$$

The empirical correlation of MacKenzie and Lichtenberger (1976), $E_f \simeq 14 kT_i$, follows if $A \simeq 1.1 \times 10^5$ in all metals.

When $\alpha \neq 0$ and $\beta \neq 0$, it can be shown that

$$E_f = \frac{(\ln A)^2}{\ln A - 2 + \epsilon} kT_i \quad (\text{A3})$$

where

$$\epsilon = \frac{F_v \beta - F_f \alpha}{F_v - F_f} [(T_0 - T_i) \ln A - 2T_i] \quad (\text{A4})$$

Since in most metals $|\epsilon| \ll (\ln A - 2)$, equation (A2) is still nearly exact. For example, in aluminium $F_v \simeq 1.11 F_r$, $A \simeq 2 \times 10^5$, $T_0 \simeq 650$ K, $T_i \simeq 540$ K and $\alpha = \beta \simeq 4 \times 10^{-5} \text{ K}^{-1}$ (Kim *et al* 1974), we have $\epsilon \simeq 0.01$ while $(\ln A - 2) \simeq 10$. Nanao *et al* (1977) define a different temperature T_v from which they obtained a correlation with E_f assuming $\alpha = \beta$. Because they expanded $F(T)$ in $1/T$, their formula is not directly applicable to the MacKenzie–Lichtenberger correlation, unlike the method of expansion in T given above. The correlation between E_f and T_i in equation (A2) is relatively insensitive to variations in A . Even when the value of A changes by a large factor, $2.5 \times 10^4 \leq A \leq 5 \times 10^5$, E_f varies by only $\pm 10\%$.

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