Temperature Dependence of Positron Annihilation in Iron and Vanadium

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Abstract. The Doppler broadened lineshape is measured as a function of temperature for iron and vanadium; vacancies produce a strong trapping effect in γ-Fe, but a weak effect in V. Threshold temperatures T_t for trapping are 1280 ± 25 and 1370 ± 30 K. Empirical linear relationships between T_t, self-diffusion energy Q^{SD} and monovacancy formation energy H_{1v}^F are discussed, and used to determine H_{1v}^F values for γ-Fe and V.

Much effort is presently being expended on studies of the temperature dependence of positron trapping in face-centered cubic and hexagonal close-packed metals, the objective being to determine monovacancy formation enthalpies H_{1v}^F. Typical recent measurements, by different techniques and using different approaches to data analysis, were described by Herlach et al. [1], Campbell et al. [2], and Dlubek et al. [3]. The behaviour of peak counting rate in angular correlation or of Doppler-broadened lineshape parameters is usually as shown schematically in Fig. 1. The strongest feature is the steep rise (C) due to vacancy trapping of positrons; this tends to saturate near melting temperature. At intermediate temperatures (B) an approximately linear behaviour is observed; this is very marked for Ni, Cu, Ag, and Au [1–3]. In some cases (e.g. [4]) the B effect gives way to a lessened temperature-dependence (A) as T is lowered further. There is debate about the origin of the pre-vacancy effects A and B, about divacancies and de-trapping at high-temperature and about other aspects. Despite a lack of consensus on these, different authors modify the basic trapping model [5] to include one or more of these in data analysis; the derived H_{1v}^F values are thus dependent on their specific assumptions.

It has been widely hoped that positron trapping could be extended to the refractory, body-centred cubic metals, where conventional techniques have provided few reliable H_{1v}^F data. We therefore report here a Doppler-broadening measurement on vanadium, which is bcc at all temperatures. Experiments on iron
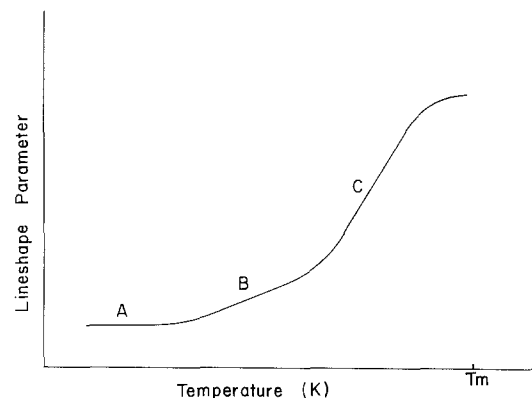

Fig. 1. Typical temperature dependence of lineshape parameter for fcc metals

are also reported. We have the following specific objectives:

a) determination of the onset temperature T_t of positron trapping in the fcc phase of iron, in order to consolidate the linear relationship between T_t and self-diffusion energy observed for fcc and hcp metals [6];

b) comparison of the onset temperature for the bcc metal vanadium with the prediction of the above empirical relation;

c) comparison of the pre-vacancy behaviour B for bcc Fe and V with that in fcc metals; in the latter there is a strong correlation with volume expansion [7, 8];

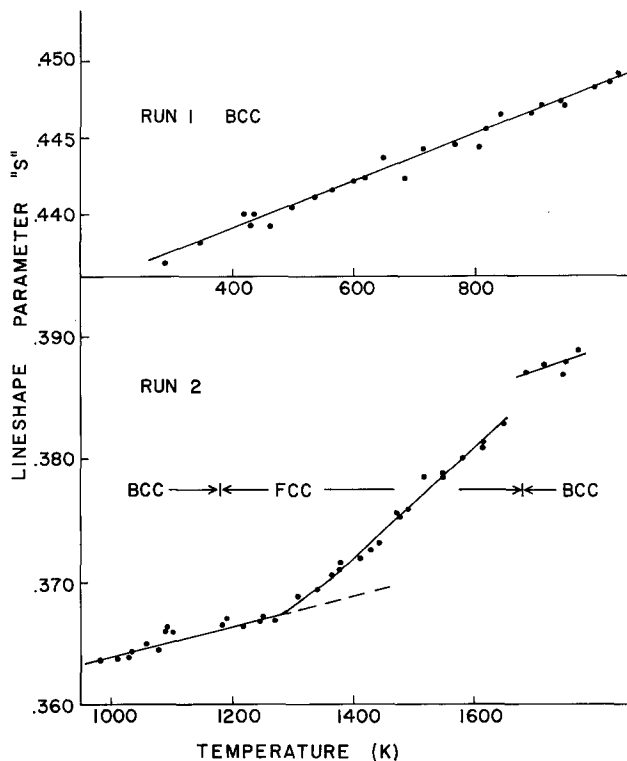d) examination of the empirical correlations between H_{1v}^F and T_t.

Fig. 2. Temperature dependence of lineshape parameter S for iron

Fig. 3. Temperature dependence of lineshape parameter D for vanadium

1. Experiment

For each metal the Doppler-broadened photon energy distribution was measured as a function of temperature using a Ge(Li) spectrometer.

The specimens were hollow cylinders (polished and etched) of length: 12.5 cm, diameter: 1.27 cm and wall thickness: 3 mm. The vanadium, whose purity was 99.99%, was supplied by the Ames Laboratory of ERDA. The iron was VP grade, 99.95% purity, from the Materials Research Corporation. Each was snugly housed in a concentric alumina tube within a cylindrical heating element, the temperature being monitored by 3 platinum-rhodium thermocouples, placed respectively at centre and end of the specimen and outside the alumina tube.

The positron source was ^{19}Ne, carried in highly purified neon gas which circulated through the specimen and through the bremsstrahlung target of a 35 MeV 100 μA electron accelerator. This technique has been described in detail elsewhere [9] and applied to the fcc metals silver and nickel [2]. The gas purification is important due to the propensity of bcc metals to take up gaseous impurities; the system included silica gel, zeolite, titanium sponge at 1220 K and, in the vanadium case, zirconium ribbon at the specimen temperature. No surface deterioration was visible to the eye after each 100-h measurement, and lineshape data were reproducible before and after heating; the purification thus appeared satisfactory.
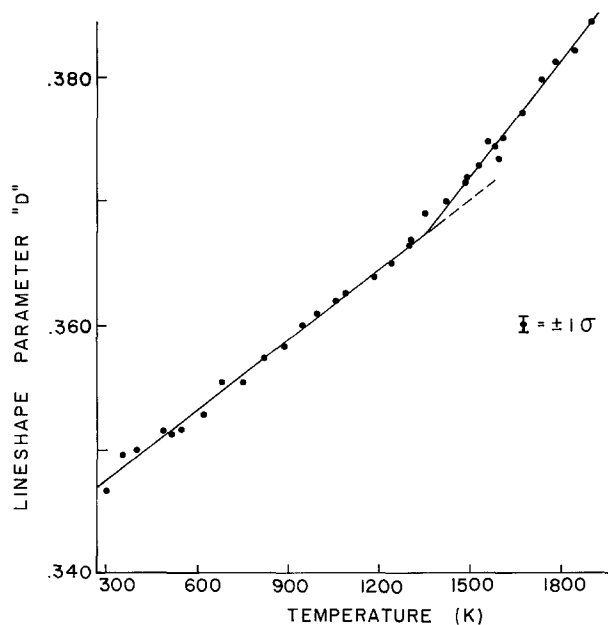
For iron the heating element provided temperatures up to 1770 K. A different element, capable of 1900 K, was used for vanadium. Prior to measurements the specimens were annealed under neon for 12 h at 1270 K and 1500 K, respectively.

A Ge(Li) spectrometer viewed the central uniform-temperature zone of the specimen through a tungsten collimator. The energy spectra of annihilation photons were recorded with a dually stabilised pulse-height analysis system. Rate variations due to accelerator changes were compensated by a ^{103}Ru source whose position was controlled by a servo-mechanism. The constancy of the ^{103}Ru 497 keV lineshape provided assurance of electronic stability.

The α-phase iron data (bcc) were taken with a Ge(Li) detector of 1.25 keV resolution at 497 keV. Unfortunately, this device developed instabilities during the γ-phase measurements. These were detected via changes in the 497 keV lineshape. The γ-iron (fcc), δ-iron (bcc) and all the vanadium data were accumulated with a second detector whose resolution was 1.5 keV. In each run reproducibility was checked by performing several temperature excursions; e.g. for vanadium measurements were performed over the four excursions 290–1770, 1770–1070, 1070–1880, 1880–500 K.

2. Data Analysis

The data were analysed in terms of lineshape parameters S, W, and D [10]. With the annihilation peak intensity normalised to unity, S is the area (typically ~ 0.4) of a central, low-momentum segment. S is the

most widely used lineshape parameter in the literature; it is crudely analogous to peak counting rate in angular correlation and reflects the fraction of annihilations that occur with conduction electrons. W is the area (~ 0.2) of two symmetric wing segments (annihilations with core electrons) and D is the difference $S - W$.

The iron data are presented in terms of the conventional S parameter. The slightly different scales used in Fig. 2 reflect merely the change in Ge(Li) spectrometer and carry no further implications. For vanadium the change in the slope of S due (presumably) to vacancy trapping was small and so we use here the slightly more sensitive parameter D; the vanadium data are given in Fig. 3.

3. Results

3.1. Iron

In run 1, the lineshape parameter S increases linearly with temperature from 293–1033 K. The slope of $(36.5 \pm 1.2) \times 10^{-6}$ K^{-1} is close to the room temperature volume expansion coefficient of 35.4×10^{-6} K^{-1}, this value is merely a convenient reference, comparison to which shows that Fe behaves similarly to the fcc metals.

In run 2, the data from 980 to 1270 K are well fitted by a straight line of slope $(34.4 \pm 2.3) \times 10^{-6}$ K^{-1}, provided one omits three high points around 825 K. We would indeed expect a continuous behaviour of the lineshape across the bcc-fcc phase change at 910 K, since the thermalised positron wavelength is spread over many atomic volumes. The three high data points at 825 K may indicate the onset of vacancies in the bcc phase; the upturn was confirmed in a separate experiment of short duration; we have insufficient data in the present work to investigate it quantitatively.

In the fcc phase the onset of trapping is sharply defined at a $T_t = 1280 \pm 25$ K. The γ-δ phase change is observed at 1400 K; since the positron is now highly localized the annihilation is sensitive to the detailed lattice structure in its vicinity.

3.2. Vanadium

Here the behaviour of each of the three lineshape parameters is well fitted by two linear segments, each having correlation coefficient $r > 0.99$. The vacancy trapping effect causes a markedly smaller slope change then one observes in the fcc metals. Trapping appears at $T_t = 1370 \pm 30$ K. Since our temperature limitation prevents us from approaching the melting point, comment on whether trapping saturates or not is impossible.

In the pre-vacancy region the slope of the S parameter is 21×10^{-6} K^{-1}; the room temperature volume expansion coefficient is 23.4×10^{-6} K^{-1}.

4. Discussion

4.1. Linear Pre-Vacancy Region

Angular correlation work by Triftshäuser [7, 8] on the fcc metals copper, silver, gold, lead, and aluminum has established that in the pre-vacancy region B, the zero angle count rate R obeys

$$R = R_0 (1 + \beta \alpha_V T),$$

where R_0 is the R value at a low reference temperature and α_V the volume expansion coefficient; the constant β ranges between 1.03 and 1.2. In Doppler work the equivalent quantity is the lineshape parameter S, and a smaller β might be expected due to the poorer resolution. For silver and nickel, we found $\beta = 0.9$ [2].

For the bcc metal vanadium, we find $\beta = 0.9$, while for the bcc phases of zirconium and titanium Hood et al. [11] found $\beta = 1.2$ and 1.0. Our value for iron is 1.03. Thus there is a little variation is β, although it does centre around the value 1.

Triftshäuser [8] claimed that region B results directly from volume expansion of the lattice, Lichtenberger et al. [12] present experimental evidence that a localization effect may be responsible, and Seeger [13] suggested self-trapping as the cause. Expression of our data in terms of the expansion coefficient does not imply a preference among these alternatives; it is simply a way of normalizing our data that may be convenient for comparison with models under development.

4.2. Weak Trapping in Vanadium

While Hood et al. [11] found no evidence for thermally generated trapping in the bcc phases of zirconium and titanium, we find a rather weak effect in vanadium. One explanation of this would be that the trapped lineshape differs only slightly from the non-trapped value; we plan to test this by a low-temperature measurement of the lineshape due to vacancies created by electron irradiation. Meanwhile, however, we have compared annealed and heavily deformed vanadium, finding that D changes by $\sim 30\%$. The explanation therefore seems unlikely.

A second possibility is that thermally activated detrapping occurs. However, the explanation that we find most appealing is the suggestion of I. K. MacKenzie that (assuming region B is due to a localization effect) for a free positron the localization probability greatly exceeds the vacancy trapping probability and that once localized the chance of transfer to a vacancy is small.
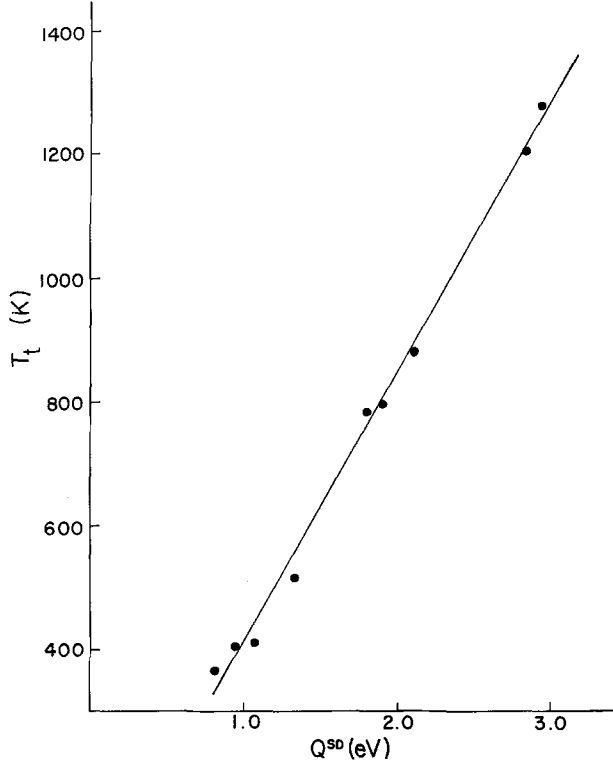
Fig. 4. Relationship between trapping threshold temperature T_t and activation energy for self-diffusion Q^{SD}

Table 1. Trapping threshold temperatures, activation energies Q^{SD} for self-diffusion and monovacancy formation energies H^F_{1v} for *fcc* and *hcp* metals

Metal	T_t [K][a]	Q^{SD} [eV][b]	H^F_{1v}[eV][c]	H^F_{1v} [eV][d]
In	323 ± 10			0.48 ± 0.01
Cd	368 ± 5	0.83 ± 0.03	0.41 ± 0.02	
Zn	404 ± 15	0.97 ± 0.03	0.52 ± 0.03	
Pb	417 ± 12	1.09 ± 0.02	0.50 ± 0.03	0.54 ± 0.02
Al	515 ± 20	1.27 ± 0.02	0.66 ± 0.02	0.66 ± 0.01
Cu	880 ± 10	2.19 ± 0.10	1.05 ± 0.03	1.29 ± 0.02
Ag	797 ± 10	1.91 ± 0.02	0.99 ± 0.03	1.16 ± 0.02
Au	770 ± 15	1.81 ± 0.01	0.92 ± 0.01	0.97 ± 0.01
γ-Fe	1280 ± 25	2.95 ± 0.06		
Ni	1205 ± 15	2.85 ± 0.10		1.73 ± 0.02

[a] Some changes from [2] reflect the increased quantity of available data in the literature.
[b] Reference [14] except for Fe, Ni, Al (see text).
[c] Values from thermal expansion measurements [14, 19].
[d] Positron trapping measurements [7, 8, 2] with linear temperature-dependence assumed for "free" positron characteristic.

4.3. The T_t versus Q^{SD} Correlation

To fit the data to the trapping model would require assumptions, empirical or theoretical, concerning the pre-vacancy effect, detrapping, etc. Given the lack of consensus on these we do not employ the trapping model here but instead extend a recent discussion on the relation between the self-diffusion energy Q^{SD} and the threshold temperature T_t (Fig. 4). MacKenzie and Lichtenberger [6] noted the existence of a linear correlation for the fcc and hcp metals copper, silver, gold, aluminum, lead, zinc, indium, and cadmium. Although this may be fortuitous it merits investigation. We have therefore reviewed the positron trapping literature and compiled best values of T_t; these are in Table 1, along with values of Q^{SD}. With the exception of nickel and γ-iron, the Q^{SD} values are those recommended by Seeger [14, 15]. That for nickel results from a literature review discussed by us elsehere [2]. For iron, results fall in two groups [16] clustering around 2.78 and 2.96 eV; the most recent study, which appears very reliable, gives 2.95 ± 0.06 eV [17].

The relationship between T_t and Q^{SD} for fcc and hcp metals is indeed linear ($r > 0.99$), being

$$T_t = (-25 \pm 23) + (432 \pm 12)Q^{SD} . \tag{2}$$

While conceding, with MacKenzie and Lichtenberger, that this is entirely empirical, we note that a similar

correlation between Q^{SD} and the melting temperature T_m is widely used. The strengthened evidence for the MacKenzie-Lichtenberger correlation may render it equally useful.

Equation (2) is founded on data for fcc/hcp lattices; the present vanadium data permit us to test its applicability to the bcc lattice. Recent work [18] on self-diffusion in single crystals yields a Q^{SD} value of 3.21 ± 0.013; this remains constant up to 1910 K, resolving an earlier debate over a possible discontinuity at 1630 K. Substitution in (2) yields a predicted $T_t = 1362$ K in good agreement with our measured value of 1370 ± 30 K. Thus (2) apparently holds for the bcc lattice also.

4.4. Vacancy Formation Energies H^F_{1v}

For the metals on which the linear relationship (2) is based, monovacancies are the chief and perhaps even the sole agents responsible for self-diffusion. MacKenzie and Lichtenberger argued that the linearity is consistent with the assumptions that H^F_{1v} is the dominant factor that determines T_t and that $H^F_{1v} = kQ^{SD}$ for the metals involved. (They discussed experimental evidence favouring a k value of 0.5.) The possibility thus arises of an empirical linear relationship between H^F_{1v} and T_t, which could provide a calibration of the present measurements on iron and vanadium (Fig. 5). Seeger [14, 19] recommended a set of H^F_{1v} values obtained from experimental comparisons of thermal expansion, as measured by x-ray diffraction and dilatometry. As can be seen from Table 1 these data favour a value of $k \doteq 0.5$. For these seven cases there is indeed a linear correlation between T_t and H^F_{1v}.
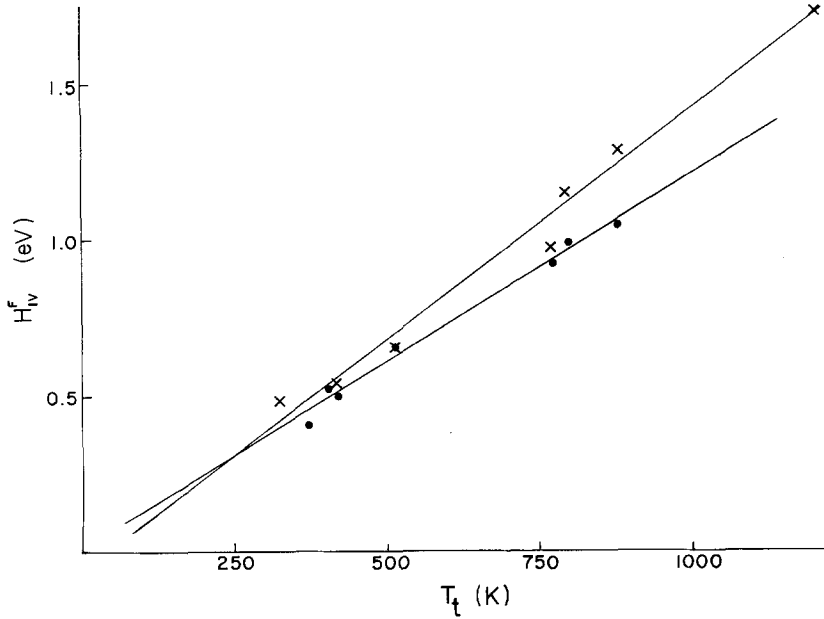
Fig. 5. Relationships between monovacancy formation energy H^F_{1v} and trapping threshold temperature T_t. Full circles represent H^F_{1v} values from [14, 19] and crosses values from [2, 7, 8]. The lines are linear least squares fits

Table 2. Results for vacancy formation and migration energies in γ-iron and vanadium

	From (4)		From (5)	
	$H^F_{1v}[eV]$	$H^M_{1v}[eV]$	$H^F_{1v}[eV]$	$H^M_{1v}[eV]$
γ-Iron	1.55 ± 0.06	1.40 ± 0.08	1.83 ± 0.14	1.12 ± 0.15
Vanadium	1.66 ± 0.09	1.55 ± 0.09	1.97 ± 0.15	1.24 ± 0.15

However, a different set of H^F_{1v} values results from an extensive set of measurements of the temperature-dependence of angular correlation by Triftshäuser and his colleagues [7, 8]. These were analysed by the trapping model (excluding detrapping, self-trapping and divacancies) with the specific assumption that the pre-vacancy effect B is directly due to volume expansion, as in (1) over both the pre-trapping and the trapping regimes. To Triftshäuser's results, given in Table 1, we add our own result for nickel [2], analysed similarly. These data also exhibit a linear correlation with T_t. Incidentally they receive some support from recent quenching experiments on copper and gold [20].

The choice between these two sets of H^F_{1v} values is controversial; each results in a set of vacancy migration energies H^M_{1v} via

$$Q^{SD} = H^F_{1v} + H^M_{1v}. \qquad (3)$$

The two sets of H^M_{1v} then favour opposing sides in the well-known controversy over the role of vacancies in stage-3 recovery [14, 21].

The two linear correlations are

$$H^F_{1v} = (0.006 \pm 0.035) + (12.1 \pm 0.6)T_t \times 10^{-4} \qquad (4)$$

using Column 4 of table, and

$$H^F_{1v} = (-0.06 \pm 0.07) + (14.8 \pm 0.9)T_t \times 10^{-4} \qquad (5)$$

using Column 5. Substitution of our measured T_t values for γ-iron and vanadium then gives the alternative results shown in Table 2 for the vacancy formation and migration energies of γ-iron and vanadium.

Conclusions

We have observed positron trapping by thermally generated vacancies in the fcc phase of iron and in vanadium, which is bcc; the trapping effect is very weak in vanadium. In preference to employing the trapping model, which offers its users the choice of several assumptions, we have simply extracted the trapping threshold temperature T_t.

The T_t value for iron is used to strengthen the evidence for a remarkably well-defined linear correlation between T_t and Q^{SD} for fcc and hcp metals; this relation holds true for the bcc metal vanadium. This correlation merits further study, but is already capable of providing Q^{SD} values through T_t measurements where conventional self-diffusion experiments are difficult.

Empirical linear correlations have also been demonstrated between T_t and H^F_{1v}. Although these need refinement, they may be used to calibrate measurements of H^F_{1v}, as done here for γ-iron and vanadium. This is no more objectionable than using the trapping

model with a wealth of parameters to be fitted, the selection of which reflects the user's assumptions. Measurement of H_{1v}^F via T_t at least has the merit of avoiding controversial high-temperature features such as divacancy trapping, saturation, temperature-dependence of trapped lineshape and detrapping. Unfortunately this approach cannot resolve the argument as to whether region B is caused by self-trapping or by thermal expansion, and thus will generate results that reflect which of these is favoured by the user.

It would be useful to have equilibrium trapping measurements done with sufficiently high counting statistics in the vicinity of T_t to permit determination of T_t from the derivative of the data. This would permit a more critical evaluation of the significance of the correlations discussed here.

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