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Vacancy formation energy for indium determined by a positron annihilation technique

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A method to determine the vacancy formation energy E_v from the measurement of the Doppler broadening of annihilation radiation is reported. The S parameter for the trapped positrons S_v that is necessary for the analysis is determined independently by using the positron annihilation age-momentum correlation technique. The method is applied to indium, whose E_v is difficult to measure by the usual Doppler broadening measurement, because the S_v is not determined clearly due to the absence of the saturation trapping of the positrons. The E_v determined is 0.48 ± 0.02 eV.

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The positron annihilation technique is one of the most powerful techniques to determine the vacancy formation energy E_v for various metals.[1]

A positron implanted into the material quickly thermalizes and annihilates with an electron with the mean lifetime characteristic to the material (typically 100–200 ps in metals). When the material contains vacancy-type lattice defects, the positron will be trapped into one of them. The momentum distribution of the γ rays from the annihilation of the trapped positrons is usually narrower than that from the positrons in the bulk because the trapped positrons have less of a chance to interact with the core electrons that have a broad momentum distribution.

As the temperature is raised, the concentration of the thermally created vacancies increases and the trapping of the positrons is enhanced. Then the observed momentum distribution becomes narrower.

If the material contains only one type of vacancies, E_v is determined through the quantitative analysis of the change in the momentum distribution by assuming the so-called two-state trapping model.[2,3] In such analysis, the line shape parameter S of the momentum distribution spectrum $N(p)$, which is defined as

$$S = \frac{\int_{\pm \Delta p} N(p)dp}{\int N(p)dp}, \tag{1}$$

is used, where Δp is a properly fixed momentum width. The S parameter satisfies the following equation,

$$\frac{S - S_f}{S_v - S} \propto \exp\left(-\frac{E_v}{k_B T}\right), \tag{2}$$

where S_f and S_v are the specific S values corresponding to the positrons in the bulk and in the vacancies, which are both usually assumed to increase linearly with temperature.[4]

In this analysis, it is necessary to heat the sample up to the temperatures where almost all the positrons are trapped into vacancies before annihilation (saturation trapping); the S parameter around these temperatures represents S_v. When the saturation trapping of the positrons does not occur even near the melting temperature, it is rather difficult to determine E_v with high accuracy since the uncertainty of S_v disturbs the result of the fitting. Indium is one of such materials. The values of E_v for this metal reported by various researchers scatter over the range of $0.39-0.59$ eV.[1]

A suggestion to use the positron annihilation age-momentum correlation (AMOC) technique[5,6] to the metals in which the trapping probability is relatively small was first made by Stoll *et al.*[7] They measured the time-selected S parameter for aluminum by using the AMOC and showed that, the temperature dependence of the S parameter for the long-lived positrons was greater than that of the time-integrated S parameter. However, they did not perform the quantitative analysis.

A method to separate the short lifetime component by using the AMOC technique was recently developed by the present authors.[8] By using this method, E_v for Zn was successfully determined only from the data in the temperature region far below the melting point. In this method, the AMOC spectrum $N(p,t)$ (the number of counts as a function of the momentum of the annihilating electron-positron pairs and the positron lifetime) is characterized in terms of the time-dependent S parameter $S(t)$, which is defined as

$$S(t) = \frac{\int_{\pm \Delta p} N(p,t)dp}{\int N(p,t)dp}. \tag{3}$$

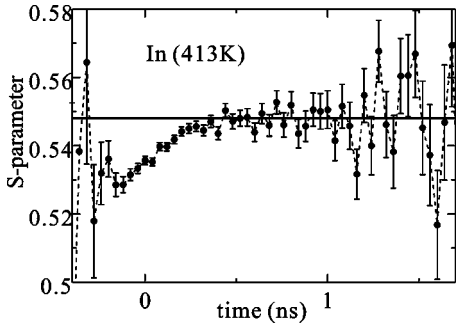

FIG. 1. Time evolution of $S(t)$ for In at 413 K.

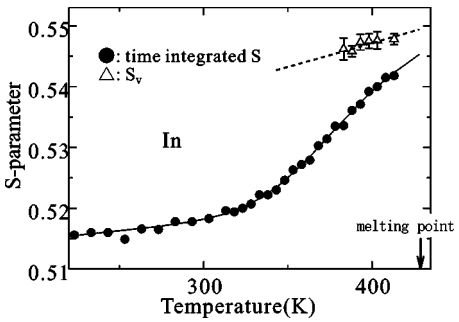

FIG. 2. *S* parameter for In plotted against the temperature.

Since the lifetime of the trapped positrons is appreciably longer than that in the bulk, S_v can be determined by the extrapolation,

$$S_v = \lim_{t\to\infty} S(t). \tag{4}$$

Using these relations the short-lived component in each lifetime spectrum was reconstructed and the E_v was determined from its temperature dependence. This method does not need the values of either S_f or S_v. It is expected to be a powerful tool for the case where the material undergoes a structural phase transition which prevents the determination of either S_f or S_v.

In the present study we develop another way of using the AMOC data and applied it to determine E_v for In. This method consists in the analysis of the temperature dependence of the ordinary time-integrated *S* parameter with the use of S_v independently determined by AMOC through Eq. (4).

The details of the AMOC system used in the present work are described elsewhere.[9] A pair of polycrystalline In specimens of four–nine purity were annealed and etched before the measurements. Five μCi carrier-free ^{22}NaCl was deposited directly on one of the specimens and covered with another. The temperature was controlled within ± 1 K by a PID temperature regulator.

Figure 1 shows the time-dependent *S* parameter $S(t)$ for In at 413 K. It is seen that $S(t)$ increases gradually with time, representing the increase in the fraction of the trapped positrons. The leveling off after 0.5 ns indicates that almost all the annihilation γ rays in this time range are from the trapped positrons, i.e., the $S(t)$ after 0.5 ns corresponds to S_v. Although the considerable fraction of the positrons still annihilate before trapping at this temperature, we can determine the S_v in this way. The solid line in Fig. 1 represents S_v. In practice, S_v was determined by fitting the theoretical function[10] predicted by the two-state trapping model to $S(t)$.

TABLE I. Reported values of E_v for In.

E_v (eV)	References
0.39 ± 0.04	Singh *et al.* (Ref. 11)
0.42	MacKenzie *et al.* (Ref. 12)
0.43 ± 0.01	Puff *et al.* (Ref. 13)
0.43 ± 0.02	Kramer *et al.* (Ref. 14)
0.45 ± 0.04	Seeger (Ref. 15)
0.48 ± 0.01	Triftshäuser (Ref. 16)
0.48 ± 0.02	present work
0.48 ± 0.03	Segers *et al.* (Ref. 17)
0.54 ± 0.03	Weiler *et al.* (Ref. 18)
0.55 ± 0.02	McKee *et al.* (Ref. 19)
0.59 ± 0.03	Rice-Evans *et al.* (Ref. 20)

The triangles in Fig. 2 show the S_v determined for the temperatures $T \geqslant 383$ K. It directly evidences that S_v is certainly an increasing function of temperature. This is probably because the size of the atomic vacancies increases along with the thermal expansion of the perfect region of the crystal. The closed circles in Fig. 2 show the *S* parameter obtained by the conventional time-integrated Doppler broadening measurements. It is seen that the *S* parameter is still increasing at the temperatures just below the melting point (429 K), as reported in previous works. The solid line and the dashed line represent Eq. (2) and a linear function simultaneously fitted to the data for *S* and S_v, respectively. The fits are good. The E_v thus determined is 0.48 ± 0.02 eV.

Table I summarizes the E_v values for In reported so far. All of them are obtained by the positron annihilation techniques except for the result of Kramer and Nölting,[14] which was obtained by the specific heat measurement. Considerable differences are seen among these values. The uncertainty of S_v due to the nonsaturation trapping even just below the melting point must have caused the scattering of the data obtained by the positron annihilation techniques. The present analysis has overcome this difficulty by employing the separate determination of the temperature dependent S_v.

In conclusion, we have developed a method to determine S_v, the *S* parameter for the positrons trapped in thermally created vacancies, at each temperature by using the AMOC technique. It has been used to determine the vacancy formation energy. The present method has greatly reduced the uncertainty in S_v which affects the reliability of the analysis. Application of this method to In has yielded a highly reliable value of E_v.

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