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Vacancy formation volume in indium from positron-annihilation measurements*

J. E. Dickman,† R. N. Jeffery, and D. R. Gustafson
Physics Department, Wayne State University, Detroit, Michigan 48202
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An equilibrium method for the determination of the vacancy formation volume in many metals is provided by the trapping of positrons at vacancies. Utilizing a Bridgman press and angular-correlation counting techniques, the vacancy formation volume in metallic indium has been determined to be 6.1 ± 0.2 cm^3/mole, or $39 \pm 1\%$ of the molar volume.

I. INTRODUCTION

In many metals, changes in the equilibrium vacancy concentration with temperature or pressure result in changes in the fundamental annihilation characteristics of positrons. Such characteristics as the positron lifetime[1] or the angular correlation of the annihilation radiation[2] are measurably different when the positrons annihilate in a vacancy compared to annihilations in the bulk lattice. Utilizing such techniques, studies have been carried out to determine the formation energies of vacancies in a number of pure metals and some alloys.[3] With the trapping-model analysis,[4,5] these results have generally been in agreement with measurements of vacancy formation energies made by other techniques, where comparisons are possible.

Using high pressure as a parameter, while holding the material at a constant temperature, measurements of changes in the vacancy concentration lead to a determination of the volume of formation of the vacancies. Because of their sensitivity to such changes, positrons offer a direct method for determining vacancy formation volumes. In the past, formation-volume determinations have been possible only by inference from high-pressure diffusion studies[6] or from nonequilibrium techniques such as quenched-in resistivity measurements.[7-9] The problems inherent in the latter measurements are many, including finite quenching speeds, divacancies and other defects present in addition to vacancies, and applicability limited to just a few pure metals. The positron technique, on the other hand, permits measurements to be made under equilibrium conditions, is more sensitive to changes in vacancy concentration in a range where divacancies are negligible, and is applicable to any metal in which positrons are trapped by vacancies. This paper presents the first measurements of vacancy formation volumes in a metal (indium) using positron annihilation. Measurements have been made by the angular-correlation technique, monitoring the zero-angle peak coincidence counting rate (ZACCR) of the annihilation radiation as a function of pressure.

II. THEORY

In a metal containing vacancies, positrons are attracted by the negative potential at the vacant site and may become trapped there.[4,5] Annihilation in such a vacancy region occurs at a different rate and with different momentum characteristics compared to annihilations in the normal metal. The measured value of the particular annihilation characteristic will be the weighted average of the free and trapped values. If F is taken as the measured characteristic (e.g., the ZACCR), F_f the value when all the positrons annihilate in the free state in the lattice, and F_v the value when all annihilate in the trapped state, then we have

$$F = P_f F_f + P_v F_v, \qquad (1)$$

where P_f and P_v are the respective probabilities of the positron annihilating "free" or trapped at a vacancy. If the rate at which positrons are trapped by vacancies is μ, the free-state lifetime of the positron is τ_f, and C_v is the concentration of vacancies, then these relative probabilities reduce to the expressions[2]

$$P_f = (1 + \mu\tau_f C_v)^{-1} \qquad (2)$$

and

$$P_v = \mu\tau_f C_v/(1 + \mu\tau_f C_v). \qquad (3)$$

The concentration of vacancies as a function of temperature and pressure is given by

$$C_v = \exp[-(\Delta E_v^f + P\Delta V_v^f - T\Delta S_v^f)/kT], \qquad (4)$$

where ΔE_v^f, ΔV_v^f, and ΔS_v^f are the activation energy, volume, and entropy of formation of a vacancy, respectively. Substituting the above expressions into the first equation yields

$$\frac{F - F_f}{F_v - F} = \mu\tau_f \exp[-(\Delta E_v^f + P\Delta V_v^f - T\Delta S_v^f)/kT], \qquad (5)$$

or

$$F=(F_v-F_f)/[1+B\exp(P\Delta V_v^f/kT)]+F_f\,, \qquad (6)$$

where

$$B=\exp[(\Delta E_v^f-T\Delta S_v^f)/kT]/(\mu\tau_f)\,. \qquad (7)$$

The free-lattice value F_f will decrease with pressure due to two effects. The first, and probably greater effect, is the changing ratio of core-to conduction-electron volumes as the metal is compressed. The angular correlation curves will therefore include a larger contribution from the high-momentum "tails" at higher pressures. Because the area under the curve is constant (proportional to the source strength), this results in a decrease of the count rate at zero angle (ZACCR). The second effect leading to a decrease of F_f with pressure is the increase of the Fermi momentum accompanying the decrease of the lattice parameter. This effect gives a broadening of the conduction-electron portion of the momentum distribution, again leading to a decrease of the ZACCR. Both of these effects are proportional to the lattice parameter, so that F_f should change approximately linearly with $\Delta l/l_0$, the compression of the lattice[10]:

$$F_f=F_0(1+\beta_p\,\Delta l/l_0)\,. \qquad (8)$$

Here, F_0 is a constant and β_p is the proportionality factor. $\Delta l/l_0$ has been measured by others as a function of pressure in indium, and over the pressure range of interest is approximately linear.[11,12] F_f can thus be taken to be linear with pressure in indium.

The pressure dependence of F_v is more difficult to determine exactly. In liquid indium, Triftshäuser[10] has found essentially zero temperature dependence for F. However, the nature of the trapping site is doubtlessly different in the liquid and solid states, so one should not expect the results to be identical. In our analysis, we have considered both the case of no pressure dependence of F_v and the case of F_v having the same pressure dependence as F_f. The reduced χ^2 fit using the latter condition was found to be significantly better than the former. We have, therefore, used this condition in our analysis. With that assumption (that F_f and F_v have the same pressure dependence) the term F_v-F_f is constant. This then gives the form for F used in fitting the data:

$$F=A_1/[1+A_2\exp(P\Delta V_v^f/kT)]+A_3+A_4P\,. \qquad (9)$$

[$A_1\equiv(F_v-F_f)$, the trapping saturation increase; $A_2\equiv B$; $A_3=F_0(1+b\beta_P)$; and $A_4=F_0\beta_P m$, with m and b defined by $(\Delta l/l_0)=mP+b$.] The vacancy formation volume ΔV_v^f was extracted by finding the best fit of F to our data using the A's and ΔV_v^f as fitting parameters.

III. EXPERIMENTAL PROCEDURES

The sample assembly consisted of two 0.35-mm-thick layers of 99.9999%-pure indium with the positron source sandwiched between them. The Co-58 positron source had been diffused into a 6-μm copper foil. The sample assembly, confined radially by a washer of gasket material (Isomica), was pressurized in a standard Bridgman press. A thin ring of steel or aluminum was required to prevent extrusion of the indium into the laminated Isomica. The temperature of the entire anvil assembly was maintained by an electric heater wrapped around the ends of the confinement vessel. The temperature was measured at two positions, near the sample and near the confinement vessel wall, with no significant difference observed.

The angular-correlation apparatus was of the usual long-slit type, with angular resolution set at 2.0 mrad. Each run began by first annealing the sample at 150 °C and atmospheric pressure, then slowly cooling to room temperature. A full angular correlation curve was taken and the apparatus set at the zero-angle peak. After pressurizing to 14 kbar, the sample was isobarically heated to within one degree of the 14-kbar melting point of indium (498 K).[13,14] During this heating process, the ZACCR was measured as a function of temperature, yielding a value of the vacancy formation energy for indium that was in good agreement with published values.[2,10] During the course of the subsequent pressurization, the temperature was held constant to within 1 °K. The increase in sample density with pressure resulted in an increased γ-ray attenuation in the sample. The ZACCR was renormalized using the single-event count rate to compensate for this effect.

IV. RESULTS AND CONCLUSIONS

The pressure dependence of the zero-angle coincidence counting rate for indium is shown for one

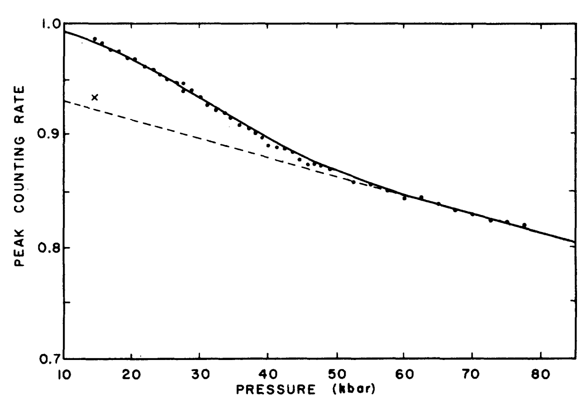

FIG. 1. Normalized zero-angle coincidence counting rate (ZACCR) vs pressure for indium.

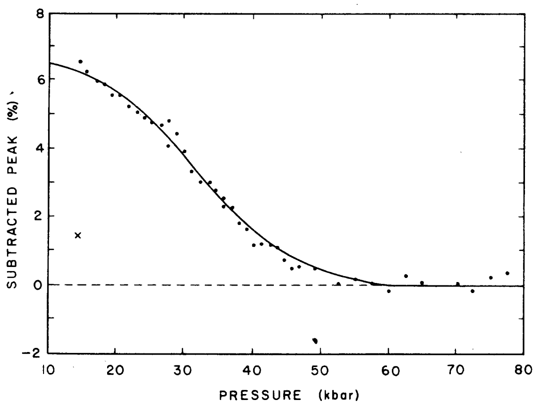

FIG. 2. Vacancy contribution of the ZACCR vs pressure for indium.

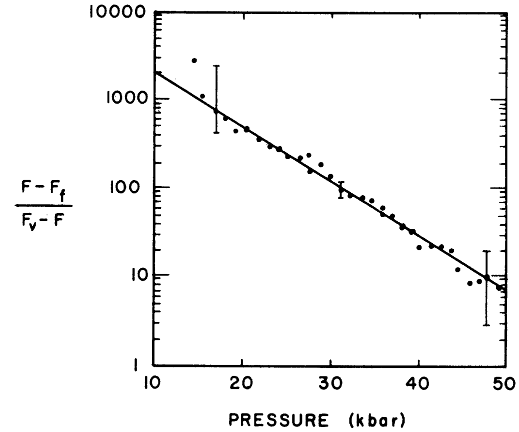

FIG. 3. Semilogarithmic plot of $(F-F_f)/(F_v-F)$ vs pressure for indium. Representative error bars are shown. Slope of the line is proportional to the vacancy formation volume.

of four runs in Fig. 1. Each point represents approximately 500 000 counts, giving a statistical uncertainty of 0.14%. The solid line is the computer fit of the function F to the data points. The reduced χ^2 value for the best fit was less than 2. The linear region above approximately 50 kbar is due to the lattice-compression contribution. The extrapolation of this to lower pressures is shown by the dashed line. The vacancy contribution, the difference between the solid and dashed lines, is shown separately in Fig. 2. The true exponential character of the data is apparent in the semilogarithmic plot of Eq. (5), Fig. 3. The slope in Fig. 3 is proportional to the vacancy formation volume. The × in Figs. 1 and 2 is the 14-kbar ZACCR measured prior to heating to 498 K. The fact that the × lies slightly above the dashed line may indicate further annealing of the sample in the course of heating to 498 K.

The vacancy formation volume in indium at 498 K was found to be

$$\Delta V_v^f = 6.1 \pm 0.2 \text{ cm}^3/\text{mole}.$$

This is 39 ± 1% of the atomic volume (15.7 cm^3/mole).[15] The error reflects the run-to-run variations, which were larger than the statistical errors within each run.

In the fitting procedure, the parameter A_2 could either be fixed according to the known formation parameters of indium,[2,10] or left free-floating. The values obtained for ΔV_v^f and β_P by these two methods were the same, within the statistical uncertainties of these quantities.

High-pressure diffusion studies in indium have yielded a value for the total activation volume (formation plus motion volumes) of 8.1 ± 0.4 cm^3/mole or 52 ± 3% of the molar volume.[16] Subtracting the two values, one obtains an estimate of the vacancy motion volume, $\Delta V_v^m = 2.0 \pm 0.5$ cm^3/mole or 13 ± 3% of the molar volume. The motion volume is thus approximately one-third of the formation volume. These results are in good qualitative agreement with studies of ΔV_v^f and ΔV_v^m in gold[7,8,17] and aluminum,[8,18] where the formation volumes were found to be about three to four times larger than the motion volumes.

The lattice-compression factor β_P was found to be about 2.8 by comparing the slope of F_f vs pressure with the lattice compression $\Delta l/l_0$ for indium from the literature. This value does not include a correction for annihilations in the source; a rough estimate of the source correction yields a value for β_P of approximately 3.1. This value of β_P lies within the range of values (3.1–3.5) for β_T, its temperature analog, reported for various pure metals including indium.[10]

In conclusion, we have used positron-annihilation techniques to measure the volume of formation of vacancies in indium. The value determined, 6.1 ± 0.2 cm^3/mole, or 39 ± 1% of the atomic volume, indicates considerable relaxation of the neighboring ions into the vacancy. Taken in conjunction with diffusion studies, these results indicate that the formation volume is about three times as large as the motional volume in this metal.

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†Present address: Physics Dept., Brookhaven Natl. Lab., Upton, N. Y. 11973.

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