Anisotropy of the positron-annihilation Doppler-broadening profiles with the crystallographic direction of Zn

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(Received 22 July 1981)

Doppler-broadened photopeaks resulting from positron annihilation in high-purity, low-dislocation-density Zn single crystals have been characterized with single-number line-shape parameters for annihilation photons emerging in the [0001] and [11$\bar{2}$0] crystallographic directions. Anisotropy of the photopeaks with crystallographic direction is observed through these parameters for sample temperatures between 183 and 568 K. The anisotropy is associated with the asymmetric nature of the positron and electron wave functions. A linear temperature dependence of the characteristic bulk annihilation parameters is deduced from data for both crystallographic directions from 183 to 568 K. The magnitude of the slope of the bulk annihilation parameters for the basal plane was found to be approximately twice that of the parameters for the [0001] direction. When the direction and temperature dependence of the bulk annihilation parameters were considered, the anisotropy of the line-shape parameters did not affect, within the precision of our data, the value of the monovacancy-formation enthalpy deduced from the two-state trapping model.

The positron-annihilation technique can be a sensitive probe of the electronic structure of metals. It is particularly sensitive to open-volume defects in most pure metals and alloys.[1] The fact that a diffusing positron can become localized at a vacancy and hence preferentially sample the electronic structure in its vicinity accounts for the technique's high sensitivity to this type of lattice defect. With positron annihilation, vacancies can be detected at atomic concentrations as low as 10^{-7}.

High-energy positrons ($E \lesssim 1$ MeV) are available from the decay of a number of radioisotopes. When a positron is emitted from one of these isotopes and enters the sample it is rapidly thermalized ($\sim 10^{-12}$ sec) by interactions with both conduction and core electrons as well as with lattice phonons. The thermalized positron will diffuse until ($\sim 10^{-10}$ sec) it annihilates with an electron. The result of this annihilation is most often ($>99\%$) two approximately antiparallel gamma photons with energies of $\sim m_0c^2 = 511$ keV.

The positron lifetime is determined by the electron density which the positron experiences. Since the electron density is lower in a vacancy than in the bulk lattice, a positron which becomes trapped at a vacancy will, on the average, have a longer lifetime than those that continue to diffuse in a Bloch-type state.

The momentum of the electron-positron pair at annihilation results in two quanta which are emitted with a distribution of small angles about π and whose energies are also Doppler shifted in the laboratory frame of reference. Positrons which are trapped and annihilate at a lattice defect (e.g., a monovacancy) produce characteristic Doppler broadening and two gamma angular correlation distributions. Similarly, positrons annihilating in the perfect lattice also produce a characteristic spectrum. The Doppler-broadening distributions

are frequently characterized by line-shape parameters whose properties have been discussed by Campbell.[2]

When applied to thermally generated monovacancies the two-state trapping model[3–5] describes any experimentally determined positron-annihilation spectra as a linear superposition of annihilation specific spectra resulting from annihilations in the bulk lattice (which are usually characterized only as being moderately temperature dependent) or at vacancies. Therefore, as the vacancy concentration increases with temperature the annihilation spectra should tend to more closely resemble that from positrons annihilating only at vacancies. Similarly, under conditions of very low lattice defect concentrations ($<10^{-7}$), the annihilation spectra should be representative of annihilations in the perfect lattice at that particular temperature.

Recently, studies have shown that for certain metals the measured parameters display more complicated behavior than that which would be expected using this simple model.[6] For example, anisotropy with crystallographic direction has been observed in the low- and high-momentum Doppler-broadening components of Cd[7] as a function of sample temperature. In the same study the very-high-momentum components exhibited behavior which is inconsistent with the application of a simple two-state trapping model. When the Doppler-broadened photopeak resulting from positron annihilation in Cd is characterized as a function of sample temperature, differences are noted between the results produced from single and polycrystalline samples.[8,9]

Monovacancy-formation enthalpies in metals are frequently determined by fitting the two-state trapping model to annihilation spectra which have been characterized as a function of sample temperature. This method obviously relies on the validity of the model. These results from Cd create some doubt about the accuracy of monovacancy-formation enthalpies which have been deduced in this manner.

In the present study the shape of the Doppler-broadened annihilation photopeaks which resulted from gamma photons emerging in the [0001] and [11$\bar{2}$0] crystallographic directions of Zn were characterized as a function of sample temperature with S and W line-shape parameters.[2] The S parameter is defined, for this study, simply as the fraction of the total counts in the annihilation photopeak which occur within a symmetric central region of the peak (511 ± 1 keV). Thus, the S parameter is dominated by annihilations with low-momentum electrons. In a similar manner the W parameter is calculated to be equal to that fraction of counts which occur in the high-momentum wing regions of the annihilation photopeak [$511\pm(2.25-7.25)$ keV]. There, annihilations occur with core and high-momentum conduction electrons. Monovacancy formation enthalpies H_{IV}^F were computed using both the threshold temperature method[10] and by fitting the two-state trapping model to the parametrized data from both directions. This was done to determine the orientational dependence, if any, on the deduced values of H_{IV}^F.

The curve-fitting process involves adjusting several potentially temperature-dependent parameters. The specific trapping rate of positrons at vacancies ν, the free annihilation rate λ_B, and the Doppler-broadening vacancy annihilation parameter S_V, were considered to be invariant. However, the temperature dependence of the Doppler-broadening bulk annihilation parameter S_B was deduced by comparing the S parameter curves which had been computed from the annihilation photopeaks from both crystallographic directions with S parameter curves which had been generated assuming that all annihilation parameters are temperature independent.

The monovacancy formation enthalpy was also deduced from positron lifetime data both for comparison with the Doppler-broadening results and to confirm the temperature independence of λ_B in the prevacancy temperature range. It should be kept in mind, however, that to compare lifetime and Doppler-broadening results is to compare two different physical measurements. The positron lifetime is a measure of the expectation value of the electron density of all momenta over the extent of the positron wave function (Bloch-like in the perfect lattice). Doppler-broadening, when analyzed in terms of a line-shape parameter, is an indirect measure of the momentum profile of electrons in a narrowly restricted momentum range.

A well-annealed 99.999% pure Zn single crystal was acid-cut so as to form two c-face ($\pm3°$) samples measuring $1.0\times1.8\times0.2$ cm^3. After polishing with a nitric acid solution the samples were annealed again in a high-purity Ar atmosphere for 18 h at 648 K and furnace cooled. The crystals were chemically etched to remove much of the surface contaminants. The basal dislocation density was estimated to be 10^6 cm^{-2} from etch pit studies[11]

performed on similarly treated Zn single crystals. A ~ 340-μCi ^{22}NaCl positron source was deposited directly on one sample and the specimens arranged in the usual sample-source-sample sandwich configuration. The source contribution to the resulting spectra was estimated, from positron lifetime measurements, to be 2% at 760 psec.

Energy measurements of the annihilation gamma photons were performed with an intrinsic Ge solid state detector (1.3 keV full width at half maximum at 478 keV). Doppler-broadening data was collected at a detector total count rate (including a ^{7}Be calibration source) of $10^4 \pm 5\%$ cps. The data collection system was software stabilized against electronic drift of the centroid of the annihilation photopeak and had a gain of 49 eV per channel. The detector was positioned in such a way that it subtended a solid angle of $\pi/25$ at a distance of 12.5 ± 0.5 cm from the Zn samples in the [0001] crystallographic direction.

Thermal gradients in the specimens, which were held together with Al foil, were minimized by placing them in a Cu container which was in thermal contact with the cold finger of a liquid-nitrogen vacuum cryostat. All measurements were performed with the specimens contained in this apparatus. Details of the heating system limited the maximum sample temperature to 568 K. Subsequent chemical analysis revealed no evidence of bulk contamination of the samples by either Al or Cu.

To further minimize the effects of drift four annihilation photopeaks instead of one were collected over a period of 1.5 h at each approximately 5 K temperature increment from 183 to 568 K. This resulted in annihilation spectra each containing $\sim 7.6 \times 10^5$ counts. The sample temperature was then slowly decreased and data collected in the same manner. No hysteretic effects were observed. Following this, the detector was similarly positioned in the [11$\bar{2}$0] crystallographic direction and the data collection procedure repeated.

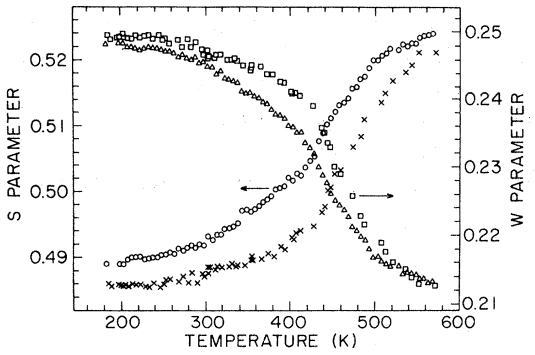

FIG. 1. S and W Doppler-broadening line-shape parameters resulting from positron-annihilation photons emerging in the [0001] ($\times$ and $\square$) and [11$\bar{2}$0] ($\circ$ and Δ) crystallographic directions of Zn. Each point depicts the average value of four data sets. The statistical error associated with each point is approximately the size of the point.

The shape of the Doppler-broadened photopeak resulting from positron-electron annihilation in Zn single crystals was characterized as a function of sample temperature from 183 to 568 K. The line-shape parameter values which appear in Fig. 1 are the average values of the parameters computed from the four photopeaks collected at each sample temperature. The entire data collection procedure was repeated with another matched detector using the same sample. These results are not presented. However, data from both detectors were found to be in good agreement.

Annihilation photons emitted in the basal plane of the sample had to penetrate ~ 4 mm more Zn than photons emerging in the [0001] direction. The additional photon scattering, caused by the width of the sample in the basal plane, produced a constant offset (-1.6% S, $+1.4\%$ W) of the values of both the S and W line-shape parameters. All data were corrected to compensate for this effect.

Subtraction of background counts from the annihilation photopeak in the manner suggested by Jorch and Campbell[12] increased the total change of the S and W parameter values between low and high sample temperature by about 5% over the results when background subtraction was not used. However, this method of background subtraction was also found to slightly alter the relationship between the S and W parameter curves from the two

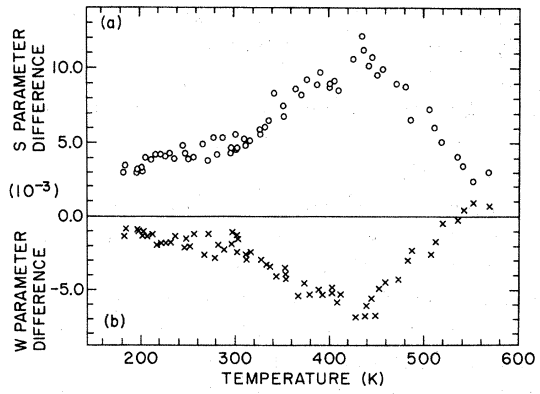

FIG. 2. Doppler-broadening line-shape-parameter-difference curves resulting from a point-by-point subtraction of the two S (a) and W (b) parameter curves shown in Fig. 1.

crystallographic directions. Background subtraction produced a relative shift in the curves which decreased the difference of parameter values in the low-temperature region and allowed the [0001] S and W parameters to attain slightly higher and lower values, respectively, than their basal counterparts at temperatures greater than 525 K. A significant anisotropy was still maintained between 300 and 525 K. Therefore, background subtraction was not used.

Figure 1 is a plot of the S and W line-shape parameters for the two crystallographic directions. An anisotropy with crystallographic direction was observed for both line-shape parameters (Fig. 1). The difference curve of Fig. 2(a) results from a point by point subtraction of the [0001] S parameter from the $[11\bar{2}0]$ S parameter. The difference between W parameters is shown in Fig. 2(b).

The line-shape parameter values as well as the slopes of both the S and W parameter curves are dependent upon crystallographic direction in the low-temperature (<300 K) region. Both difference curves exhibit a small slope, the absolute value of which abruptly increases at 300 K.

In the so-called "prevacancy" region, approximately 300 to 400 K, a suggestion of a second slope is observed in the basal line-shape parameters the magnitude of which is intermediate between that in the low-temperature and vacancy (400–525 K) regions. A smaller slope is evidenced in the [0001] S parameter in this temperature range and a slight prevacancy effect occurs in the high-momentum [0001] parameter as well.

The S parameter for the $[11\bar{2}0]$ direction attains a larger value than does the [0001] S parameter in the high-temperature (>525 K) region. However, in the same temperature regime the [0001] W parameter and its basal counterpart have approximately the same value. This can most easily be seen in the difference curves of Fig. 2. The same figure shows the anisotropy of line-shape parameters with crystallographic direction to be greatest in Zn at $\sim$ 435 K.

Lifetime and single-direction Doppler-broadening data were collected on the same Zn samples down to 10 K. After subtraction of a source component the curve that resulted from fitting a single term to the lifetime spectra remained constant, within the statistical precision of our data, for temperatures below 360 K. The S and W line-shape parameters maintained small but constant positive and negative slopes, respectively, in the same temperature region. In some metals an increase of the trapped positron lifetime component[13] and S parameter values[9] with decreasing temperature have been observed at low temperatures. This increase is indicative of shallow traps which cannot substantially effect positron behavior until the thermal energy of the positron is lowered sufficiently by cooling the sample. No evidence of this type for the existence of shallow traps in these single-crystal Zn samples was observed down to 10 K. No prevacancy effects were detected in the lifetime results when a single decay term and source term were fitted to the positron lifetime data in the prevacancy region.

The two-state trapping model was fitted both to the lifetime data and Doppler-broadening results. Temperature-dependent line-shape parameters were used to characterize annihilations in the bulk crystal. The linearly increasing S parameter, observed here (Fig. 1) in the low-temperature region for single-crystal Zn, is similar to that seen in Doppler-broadening data from single-crystal Cd,[9] in polycrystalline Cd lifetime data,[14] and in Doppler-broadening data from polycrystalline Zn.[9] The experimentally determined S parameter is presumed to be a weighted linear combination of characteristic vacancy S_V and bulk S_B annihilation parameters defined by Eq. (1),

$$S(T)=\frac{S_B(T)+(\kappa/\lambda_B)S_V}{1+\kappa/\lambda_B}\ , \tag{1}$$

where $\kappa=\nu e^{S_{IV}^F/k}e^{-H_{IV}^F/kT}$ is the vacancy trapping rate, ν is the specific vacancy trapping rate, S_{IV}^F is the monovacancy formation entropy, and H_{IV}^F is the monovacancy formation enthalpy. λ_B is the annihilation rate of free (Bloch-state) positrons in Zn and k is Boltzmann's constant. As previously mentioned, λ_B ($=6.40\times10^9$ sec^{-1}) was found to be constant in the temperature region below that at which vacancy trapping becomes measurable and for the sake of this analysis it was assumed that all annihilation parameters except S_B are invariant. $\nu e^{S_{IV}^F/k}$ was determined to be

$$0.8\times10^{15}\pm0.2\times10^{15}\ \text{sec}^{-1}$$

and

$$1.9\times10^{15}\pm1.0\times10^{15}\ \text{sec}^{-1}$$

from the positron lifetime and Doppler-broadening data, respectively. The latter value was used in the following analysis.

Equation (2) describes a hypothetical S parameter curve for which all annihilation parameters are

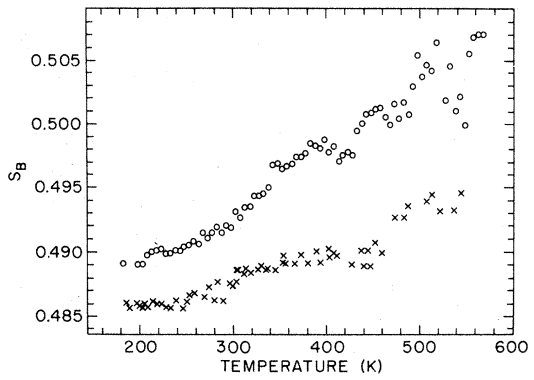

FIG. 3. Temperature dependence of the Doppler-broadening bulk annihilation component resulting from the application of Eq. (3) to S parameter data from the [0001] ($\times$) and [11$\bar{2}$0] ($\circ$) crystallographic directions.

independent of temperature,

$$S'(T)=\frac{S'_B+(\kappa/\lambda_B)S_V}{1+\kappa/\lambda_B} . \quad (2)$$

Subtracting Eq. (2) from Eq. (1) and rearranging terms results in Eq. (3) describing the characteristic bulk annihilation parameter,

$$S_B(T)=[S(T)-S'(T)](1+\kappa/\lambda_B)+S'_B . \quad (3)$$

This equation and the S parameter data in Fig. 1 produce the points shown in Fig. 3. Figure 3 depicts a positive linear temperature dependence of the bulk annihilation parameter $S_B(T)$. The oscillation in the curves of S_B between 300 and 500 K are not thought to be significant. The scatter is thought to be an artifact of the method of analysis. A linear least-squares fit to the results in Fig. 3 produces a slope for the basal parameter 2.1 times that of the slope of its [0001] counterpart. The W line-shape parameters were analyzed in the same way and a linear temperature dependence of the bulk annihilation parameter $W_B(T)$, analogous to that for $S_B(T)$, was deduced. The magnitude of the slope for the basal W parameter was found to be 1.7 times that of the [0001] $W_B(T)$.

Equation (1) was fit to the Doppler-broadening data of Fig. 1 with $S_B(T)=S_B(T=0\text{ K})+A_S T$. The values for A_S were held constant during the analysis at the values determined by Eq. (3). The slope of the basal bulk annihilation parameter was fixed at 4.7×10^{-5} K^{-1} and the slope of the [0001] bulk S parameter was set equal to 2.2×10^{-5} K^{-1}. Equation (1) was modified for W parameter analysis by replacing $S(T)$ with $W(T)$, S_V with W_V, and $S_B(T)$ with

$$W_B(T)=W_B(T=0\text{ K})-A_W T .$$

When this modified equation was fit to the W line-shape parameter data A_W was set equal to 2.6×10^{-5} K^{-1} for the [0001] parameter and 4.4×10^{-5} K^{-1} for the basal parameter. This fitting procedure resulted in a monovacancy formation enthalpy H^F_{IV} deduced from basal line-shape parameters of 0.50 ± 0.02 eV and from [0001] parameters of 0.51 ± 0.02 eV. Threshold temperature analysis resulted in the H^F_{IV} values of 0.47 ± 0.06 eV ($T_T=375$ K) from the basal parameters and 0.49 ± 0.06 eV ($T_t=389$ K) from [0001] parameters. We define T_t by the intersection of a straight-line approximation to the prevacancy and vacancy trapping sections of the parameter-versus-temperature curve. These values are in agreement with those extracted using the fitting procedure. The positron lifetime data produced a value of $H^F_{IV}=0.51\pm0.01$ eV. Removing from consideration those data points which occur within the prevacancy temperature range had only a small effect on the resulting values of H^F_{IV}.

At the present time the prevacancy effect is not well understood. Several possible causes have, however, been suggested. Seeger has proposed positron metastable self-trapping.[15] Stott and West[16] have suggested a combination of thermal expansion and lattice phonons as the cause of the prevacancy effect. Here, changes in the positron wave function with temperature are most simply described as changes in the weighting of the positrons high-momentum components (HMC) with the major effect occurring in the (0002) HMC. MacKenzie[17] has suggested that zone-boundary phonons may provide transient lattice dilations large enough to cause positron localization and that in anisotropic metals such as Zn and Cd the direction of propagation might be important. The data presented here for Zn show, for the first time, a directionally dependent prevacancy effect in single-crystal Zn. This should aid in the determination of the cause of the prevacancy effect since it has now been demonstrated that the prevacancy effect occurs in Zn as well as Cd single crystals[7] and that the effect is dependent upon crystallographic direction.

The shape of the prevacancy region observed in one crystallographic direction of Cd (Ref. 7) is suggestive of some type of activated process. Making this assumption, Jean *et al.*[7,18] deduced an activation energy of 0.08 ± 0.02 eV. However, the prevacancy region in our data appears to be linear with

a slope intermediate between that exhibited by the low-temperature and vacancy regions. The onset of the prevacancy effect in both Cd and Zn occurs approximately at the Debye temperature of these metals. This, however, seems to be largely coincidental since the Debye temperature bears no similar relationship to the prevacancy effect in other metals.

As previously mentioned the value of the S parameter, in the high-temperature (>525 K) region, is greater for the $[11\bar{2}0]$ direction than for the [0001] direction. The difference of parameter values in this temperature range is small ($<2\sigma$). However, this difference may reflect the anisotropy of the positron-electron momentum distributions in a vacancy. In this case high-precision angular correlation measurements could be useful for investigating the electronic structure at vacancies.

The results of this study demonstrate that, when characterized in terms of line-shape parameters, the Doppler-broadened positron-annihilation photopeak from Zn does not behave in a manner consistent with the simplest notion of a two-state trapping model composed of invariant annihilation parameters. It was shown that S_B and W_B are dependent not only on sample temperature but also on crystallographic direction. When S_B and W_B were varied in this manner the value of H_{IV}^F deduced by fitting the two-state trapping model to our data was found to be independent of crystallographic direction within statistical error. High-precision angular correlation or two-detector Doppler-broadening[19] studies would seem to be called for in order to help determine the origin of the prevacancy effect.

ACKNOWLEDGMENTS

Appreciation is extended to W. Frieze and H. H. Jorch for experimental assistance and to A. N. Goland for his continued interest and support. We would also like to acknowledge several useful discussions with R. N. West and I. K. MacKenzie. This work is partially supported by the U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

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