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Temperature dependence of the Doppler-broadened positron annihilation spectra in single and polycrystalline Cd

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The Doppler shifts of annihilation photons have been measured in well-characterized single and polycrystalline samples of Cd as a function of sample temperature betewen 10 and 540 K by a two-detector Doppler-broadening method which permits separation of core-state and valence-state annihilations. The temperature dependence of the broadening associated with those annihilations involving predominantly low-momentum electrons was found to be dependent on the orientation of the single-crystal sample with respect to the axis of the two detectors. This detected anisotropy at various sample temperatures ($220 \leq T \leq 325$ K) is thought to be associated with the asymmetric nature of the positron and electron wave functions, possibly localization of the positron. The variation with crystallographic direction in the low-momentum region occurs both at low temperatures in the so-called prevacancy region and at temperatures where vacancy trapping is observable. The components of the Doppler-broadened spectra that correspond to annihilations with very-high-momentum electrons as might be expected do not show this orientation dependence although they agree with the low-momentum components in implying the existence of a well-defined prevacancy region.

I. INTRODUCTION

In recent years positron-annihilation techniques have been increasingly utilized in studying the electronic properties of both imperfect and defect-free materials.[1] Positrons which are readily available from a number of different radioactive sources, are implanted in the samples of interest. After implantation the positron thermalizes in approximately 10^{-12} sec and diffuses until it annihilates (0.1–0.3 nsec) with an electron in the metal, a process predominantly characterized by the emission of two photons. Owing to the momentum of the electron, the two quanta are emitted in a narrow distribution of angles about π and the photon energies are Doppler shifted in opposite senses in the laboratory frame. The positron lifetime is determined by the electron density at the site of the positron.

Over the last decade positrons have been shown to be extremely sensitive in detecting vacancy-type defects with atomic concentrations above 10^{-7} and have been employed extensively to deduce vacancy-formation enthalpies in many metals.[1] Positrons localized at these vacant lattice sites experience a lower average electron density, hence a longer lifetime, and a characteristically different electron momentum distribution. Each of these quantities is experimentally distinguishable from its value in the perfect lattice. Recently with more precise experiments it has been found that the measured parameters exhibit more complicated behavior than that described by a simple two-state model (annihilation either in the perfect lattice or in a vacancy) when vacancies are generated by heating the sample.[2–5] The two-state trapping model is difficult to apply because an anomalous behavior occurs in some metals below the temperature region where a detectable fraction of positrons is localized in thermally generated vacancies. This is commonly referred to as a "prevacancy region."[2] At present there is no quantitative understanding of the "prevacancy effect," although Seeger has suggested a metastable self-trapping state for the positron in this temperature region.[6] Subtraction of the data in this prevacancy region seriously affects the deduced value of the vacancy formation enthalpy.

With the present technique of using two Ge detectors in coincidence, it is possible to obtain momentum spectra over five orders of magnitude in intensity as opposed to the two orders of magnitude covered by conventional single detector methods. This capability permits a comparison between the low- and very-high-momentum regions of the resulting spectra to be made. In previous studies of this very-high-momentum region in Al (Ref. 7) and Ag (Ref. 8) no indication of the prevacancy effect was observed, and hence a simple application of the two-state trapping model to the very-high-momentum region was made to obtain an accurate measurement of the vacancy formation enthalpy. The low-momentum regions in Al (Ref 7) and Ag (Ref. 8) do exhibit the prevacancy effect contrary to the very-high-momentum region in these same metals.

Cadmium has proved to be one of the more complicated systems with respect to the interpretation of the results of momentum spectra as determined by positron annihilation techniques. Several researchers have reported measurements of the positron lifetime,[4] Doppler broadening,[2,3] and angular correlation[4] as a function of sample temperature with somewhat varying results.[2–5] In general, the data can be separated into three regions. The first region encompasses those data below 170 K where the experimental parameters are almost temperature independent in a high-purity well-annealed Cd crystal. The second region extends from approximately 170 to 350 K, is associated with the prevacancy phenomenon,[6] and cannot be explained fully by simple thermal expansion of the lattice. At most, expansion can only account for 50% of the experimental change in this temperature region. To add to the complexity, this region does not appear linear, especially in single crystals, where a plateau was observed between 280 and 310 K in the parameters determined by Doppler-broadening measurements.[5]

In region three, above 350 K, positron trapping at thermally generated vacancies becomes observable, and leads to the familiar S curve. In the present study on both oriented single crystals and polycrystalline Cd samples of high purity our intent was to determine with the two-detector technique whether the low- or very-high-momentum regions of the resulting spectra showed any crystal orientation dependence, and further, whether the very-high-momentum regions, previously unstudied, fail to exhibit a prevacancy region as was the case for Al (Ref. 7) and Ag (Ref. 8).

II. EXPERIMENTAL DETAILS

The essence of the present technique is to use two Ge detectors in collinear geometry to detect both quanta from the annihilation event with time coincidence and energy selection. The present study uses only the energy difference of the annihilation quanta $\Delta E = E_2 - E_1$ where E_1 and E_2 are the individual photon energies. The energy difference ΔE is defined by $\Delta E = \vec{p} \cdot \vec{c}$ where $\vec{p}$ is the electron-positron momentum in the laboratory system and $\vec{c}$ is the velocity of light in the direction of the photon with energy E_2. A measurement of ΔE thus determines the projection of the momentum $\vec{p}$ along the photon direction. The great advantage of the two detector method is in the investigation of the very-low-intensity high-momentum components. In the present experiment the time coincidence and energy selection produces a peak to background ratio of approximately 10^6, thus making the measurements in the very-high-momentum regions feasible. A more detailed explanation of the present system has been published elsewhere.[9] The experimental details of the furnace and cryostat are identical to those described in an earlier publication.[8]

Two single-crystal samples ($10 \times 15 \times 1.5$-mm thickness) were acid cut, polished, and etched from a 99.9999%-pure Cd low-dislocation-density crystal,[10] and the polycrystalline Cd sample was of 99.999% purity. The c axis was found to be $\sim 15°$ off the normal to the surface on both single crystals as determined by x-ray diffraction. A 30-μCi ^{68}Ge positron source was electroplated on a 0.0089-mm-thick light-tight Ni foil,[11] and sandwiched between two similar Cd crystals. The contribution from annihilations in the source and Ni foil was estimated to be less than 2% of the total measured intensity. After insertion of the source between the samples, the sandwich was wrapped with alumina-silicate wool and Al foil in order to minimize strain introduced by handling. The container holding the sample and source was then annealed at 575 K for 24 h in ultra-high-purity Ar before any measurements were made. The low-temperature and high-temperature measurements were made in high-purity He and Ar atmospheres, respectively. The data were recorded in the sequence of 10 to 325 K after which the samples were transferred to the furnace for measurements ranging in temperature from 298 to 540 K. The procedure was then reversed to permit observation of any hysteresis. After the experimental run the Cd single-crystal samples were again checked with x rays to verify that no recrystallization had occurred during the experiment. The sample surfaces were also checked with an optical microscope and the areal density of cavities on the surface was less than 10^{-4}. The mass density of the Cd was measured to be 8.63 g/cm^3 as compared to the theoretical density of 8.65 g/cm^3 therefore determining that no large amounts of occluded gases were contained in these samples. The presence of occluded gases which can form bubbles in Cd could be a factor in explaining why some disagreement has been found among various positron studies.[12]

III. RESULTS AND DISCUSSION

The experimental spectra were normalized to one over the interval from -30 to 30 keV, i.e.,

$$\int_{-30}^{30} P(\Delta E)\, d(\Delta E) = 1 \ .$$

In this expression ΔE is the energy difference between the two annihilation photons and $P(\Delta E)$ is the probability that the two photons have a difference energy ΔE. The measure of P is taken to be the number of coincidence counts in an interval $d(\Delta E)$ around ΔE.

The temperature dependence of the quantities

$$S(T) = \int_{-1}^{1} P(\Delta E)\, d(\Delta E)$$

and

$$W(T)=\int_{-30}^{-5.4}P(\Delta E)d(\Delta E)+\int_{5.4}^{30}P(\Delta E)d(\Delta E)$$

are shown in Figs. 1 and 2 for $10 < T < 540$ K. The quantities S and W represent the low- and very-high-momentum regions, respectively. These quantities were selected by analogy to those commonly discussed by others[1] using the conventional single detector Doppler broadening method. The quantity $S(T)$ is weighted by the contributions from the low-momentum d electrons and the conduction electrons whereas the contribution from the deep-core electrons is very small. The very-high-momentum events, $W(T)$, are due predominantly to deeply bound core electrons and can be adequately described by the independent-particle model (IPM).[7,13] The IPM[1] has been calculated for Cd as described by Lynn *et al.*[6] where single-particle wave functions describe the electron and positron.[1] The wave functions used in those calculations were obtained from numerical integration of the Schrödinger equation based on a potential corresponding to a spherical average of overlapping atomic electron densities.[14] A measured positron lifetime of 186 psec was used for the comparison. Good agreement was obtained between the theoretical predictions and the data beyond 5 keV when the $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ shells were included. The $4d^{10}$ electrons were not included in the calculations as an abrupt truncation of the spatial distribution at the surface of a sphere introduces spurious high-momentum components. The IPM satisfactorily reproduces both the shape and absolute intensities of the experimental high-momentum tails beyond 7 keV. An important feature to be noted concerning the very-high-momentum region is that a change in the potential at large distances from the nuclei results in a change in the absolute value of the very-high-momentum annihilation rates, but the momentum dependence of these events is expected to be largely unaffected. This was found to be the case in earlier studies in the case of Al and Ag.[7,8] The very-high-momentum curves measured for an untrapped and a trapped positron are nearly identical in shape but the latter is significantly reduced in intensity. Therefore $W(T)$ is produced from a set of

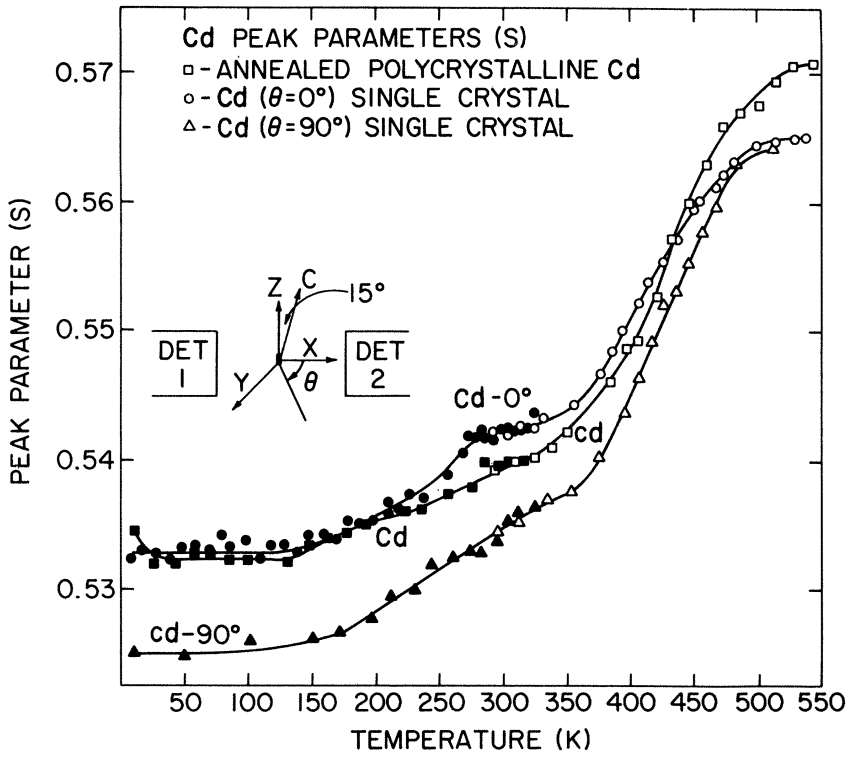

FIG. 1. $S(T)$ vs temperature (K) for high-purity single crystal and polycrystalline Cd. The quantity $S(T)$ is summed in the region of ΔE from ±1.0 keV about $\Delta E = 0$ in the Doppler-broadened spectra. The 99.9999%-pure Cd single crystal is oriented 15° off of the c axis relative to the z axis. The 90° rotation was made about the z axis. The curve labeled Cd represents a well-annealed 99.999% purity Cd polycrystal. The solid points are those data taken in the cryogenic system and the open points were obtained when the sample was in the furnace. Owing to the scattering of the γ rays in the different systems, the data for each set have been normalized in the overlap temperature range (298–350 K). The statistical errors (2σ) are about the same size as the points on the plot. The solid line is drawn as a guide to the eye.

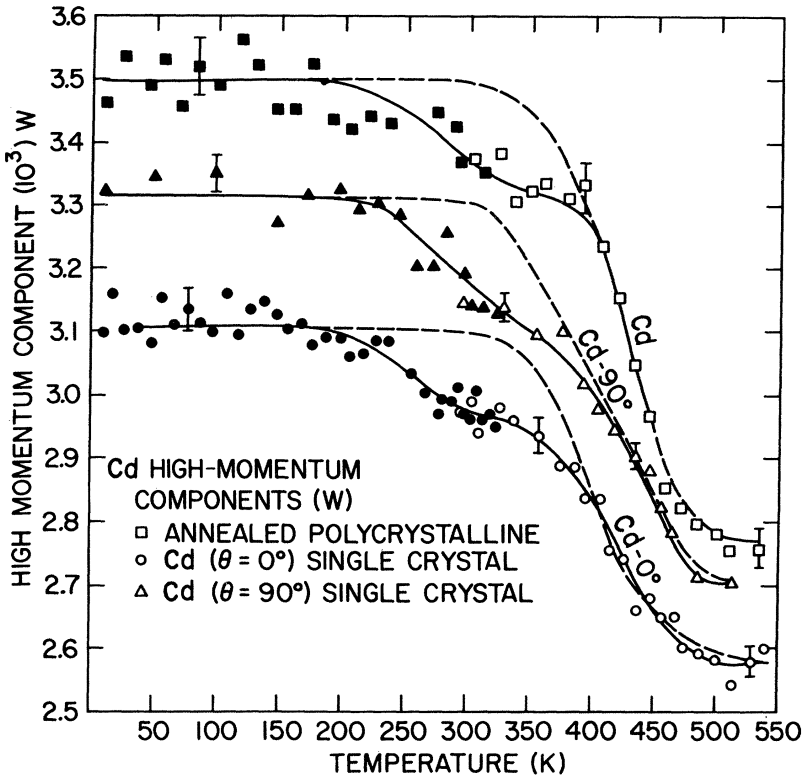

FIG. 2. $W(T)$ vs temperature (K). The curves are labeled in the same way described in Fig. 1. The high-momentum events are summed in ΔE between ±5.4 and ±30 keV about $\Delta E = 0$ in the Doppler-broadened spectra. The error bars shown are representative of 2σ. The solid lines are a guide to the eye whereas the dashed lines are the theoretical values generated from the two-state trapping model, with a vacancy formation enthalpy of 0.52 eV.

parallel curves in which the intensity is reduced with increasing sample temperature (Fig. 2), owing to positron trapping at thermally generated defects. Currently, it is thought that any trapping centers will reduce $W(T)$ relative to its magnitude when all annihilations occur in the perfect lattice.

The 99.9999%-pure Cd single crystal is oriented 15° off the c axis relative to the z axis. A 90° rotation was made by a rotation about the z axis (Fig. 1). The curve labeled Cd depicts the annealed polycrystalline results. As previously mentioned, these curves can be separated into three regions, 10 to 150 K, 150 to 330 K, and 330 to 540 K, each of which has a different shape and slope. The low-temperature region is almost temperature independent and in good agreement with other studies.[3,5] The onset temperature of the regions is not always clearly defined and some variation has been found among different experimental studies.[2–5] The increase in S at the lowest-temperature point (10 K) on the curve representing the polycrystalline sample is probably associated with some shallow defect still remaining in the lattice after annealing. All of the present data were taken on high-purity well-annealed crystals and, therefore should be typical of crystals that have low concentrations of nonequilibrium defects. In order to take account of possible variations in photon scattering in the sample chambers for low- and high-temperature measurements all the curves were normalized in the temperature region where data taken in the cryostat and in the furnace overlapped. Differences in the absolute values of $S(T)$ and $W(T)$ between the three curves are thought to be partially attributable to different photon scatterings in the samples and fixtures, although a systematic change with temperature is found which cannot be solely associated with scattering of the photons. Figure 3 shows a point-by-point subtraction of the $S(T)$ data for two orientations of the single crystals at various temperatures. Whereas $\Delta S(T)$ has a minimum occurring around 280 K and subsequently increases with increasing temperature, $\Delta W(T)$ exhibits no systematic behavior which can be similarly characterized. The variations in the temperature dependence of the low-momentum electrons show that significant anisotropies exist between the crystallographic orientations. The observed directional variation in the temperature dependence at the higher temperatures (350–525 K) reflects the anisotropy of the positron and electron wave functions while the positron is lo-

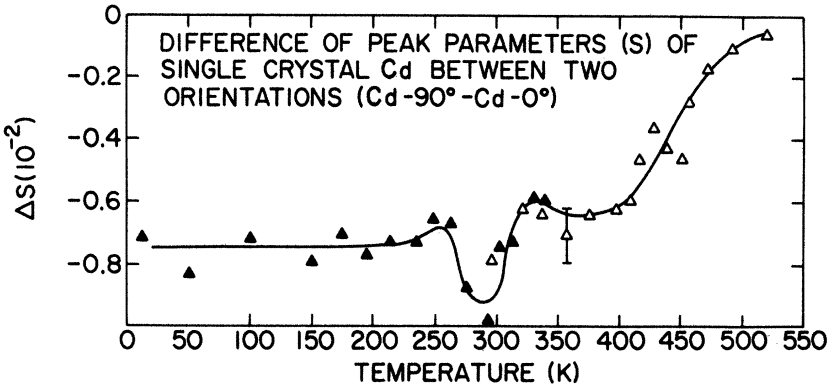

FIG. 3. A point-by-point subtraction of $S(T)$ vs temperature (K) is shown for the two different crystallographic directions measured for the Cd single crystal. The typical error is shown in the figure. The solid line included is drawn as a guide only.

calized at a monovacancy.

If the region extending from 270 to 350 K is neglected, different slopes can be deduced by fitting a straight curve to $S(T)$ vs T in the intermediate region extending from 200 to approximately 325. For Cd-0, Cd-90, and Cd (Fig. 1) the values of 94×10^{-5}, 117×10^{-5}, and 65×10^{-5} K^{-1} are extracted, for the slopes between 170 and 325 K, respectively. The slopes have been defined as $\Delta S/S_0 T$ where S_0 is the low-temperature value. The variation in slope also produces systematic changes in the threshold temperature which in many cases is employed as an empirical method of deducing the vacancy formation enthalpy. On the basis of the method described by Mackenzie and Lichtenberger[15] a 16 K variation is found in this onset temperature between the different orientations. This orientation dependence of the prevacancy region would make the correct determination of the prevacancy temperature dependence difficult which is necessary for accurate measurements of the vacancy formation enthalpy. One should also realize the need from these results to use single-crystal specimens when studying vacancies with either the Doppler broadening or angular correlation technique. Within the statistical error, the quantity $W(T)$ seemed to behave similarly between the different Cd crystals as shown in Fig. 2.

The most striking difference in $S(T)$ vs T between the two crystal orientations is the plateau for the Cd-0 crystal extending over the temperature range from 270 to 325 K, and missing for the Cd-90 crystal. This plateau region was first clearly observed by Rice-Evans *et al.*[5] in a study on a single crystal of Cd of unspecified orientation. The observed difference in $\Delta S(T)$ around 298 K is thought to be associated with the anisotropy of the positron-wave function as exhibited only by the low-momentum quantity, $S(T)$ (Fig. 3). The shape of the high-momentum tails should be nearly independent of temperature whether or not the positron is trapped.[7] If the positron is localized, the very-high-momentum components will be simply reduced in intensity. As was shown in earlier studies[7,8] of Al and Ag the integrated region of the very-high-momentum components, $W(T)$, remained flat with temperature until the onset of a detectable amount of positron trapping at thermally generated monovacancies occurred. The changes (Fig. 2) in the quantity, $W(T)$, between 200 and 350 K are identical within statistical accuracy among the different samples, and therefore are thought to be associated with some type of trapping of the positron in the lattice before the onset of a detectable effect arising from positron localization at vacancies. The general shape of the curve in this region shows indications of an activated process associated with the localization. If this region is treated in a manner similar in nature to that predicted by the two-state trapping model one obtains an activation energy of approximately 0.08 ± 0.02 eV. Smedskjaer *et al.*[4] have also fitted this region in a similar manner on a polycrystalline sample and have found an activation energy of 0.13 ± 0.02 eV. Our deduced energy does depend slightly on the crystallographic direction. This procedure is not guided by a physical picture; however, it does provide a method of removing the prevacancy background from the curves of $W(T)$ in a reasonably well-defined manner. Seeger's[6] model was not fitted to the data owing to the lack of statistical precision in the data.

If the prevacancy region is ignored or subtracted from the curve one obtains a vacancy formation enthalpy of 0.52 ± 0.05 eV. The predicted curves are shown as dashed lines in Fig. 2. The derived formation enthalpy is close to the reported values which range from 0.4–0.5 eV.[1] It should also be mentioned that no hysteresis was found in this region on subsequent runs with either increasing or decreasing sample temperature. This leads one to believe that the

observed behavior is an intrinsic property of Cd and is probably not associated with shallow traps, i.e., dislocations, subcells, or grain boundaries.

IV. CONCLUSIONS

Our analysis of the data shows that even with well-characterized Cd, the very-high-momentum region does not fit a simple two-state trapping model, in contrast to Al (Ref. 7) and Ag (Ref. 8) studied by this technique. The behavior of the very-high-momentum region versus sample temperature is thought to be associated with an intrinsic property of the Cd and not impurities or nonequilibrium defects.[16] Anisotropy is observed in the low-momentum region with different crystal orientations, and even larger differences are expected between the c and a axis than those observed in these studies. The low-momentum region is found to have a strong temperature dependence with different crystal orientations even in the region dominated by thermally generated vacancies. Further high-temperature studies associated with the angular dependences of single-crystal samples in the low-momentum region should allow researchers to map out the general shape of the positron and electron wave functions while a positron resides at a vacancy.

We hope this paper will inspire some new theoretical investigations aimed at understanding the complicated behavior of the quantities $S(T)$ and $W(T)$.

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