Temperature dependence of the Doppler-broadened spectra in Ag obtained by positron annihilation

Y. C. Jean, K. G. Lynn, and J. E. Dickman*
Brookhaven National Laboratory, Upton, New York 11973
(Received 16 October 1979)

Doppler-broadened spectra have been measured in well-annealed high-purity polycrystalline silver as a function of temperature between 9 and 1098 K by a two-detector Doppler-broadening positron-annihilation technique. Those positrons which annihilate with high-momentum core electrons exhibit a larger fractional change in intensity than those which annihilate with the low-momentum electrons when positron trapping at vacancies occurs. The probability of annihilation with the high-momentum core electrons remains constant as a function of temperature before positron trapping at vacancies is detected. The vacancy-formation enthalpy obtained by applying the two-state trapping model to the high-momentum spectra is 1.11 ± 0.05 eV. The importance of utilizing high-momentum spectra for extracting vacancy-formation enthalpies is discussed, and a new structure is observed in the curves of the ratio between the high- and low-temperature momentum spectra.

I. INTRODUCTION

A positron implanted into condensed matter is known eventually to thermalize and annihilate with an electron, which results in the emission of γ rays. The dominant decay mode in metals is by the emission of two photons, and by measuring the energies and relative emission angle of these photons one can extract information concerning the electrons residing in the metal.[1] Since the positron is positively charged, one finds that most of the annihilations occur with the outer or conduction electrons. With a recently developed two-detector Doppler-broadening technique[2] it is possible to observe those annihilations which occur with deeply bound core electrons, which have not been studied because of low intensity, background, and counting-rate problems. Thus the main advantage of the two-detector Doppler-broadening (2-D) technique is in the assessment of the high-momentum-electron contribution[2,3] which can be described by simple theory.[4] When used as a supplement to angular-correlation data, this high-momentum information provides a means of fully understanding the positron dynamics in metals, which will help provide useful information on the electronic structure of metals.

The Ag system was chosen for study because of the relatively high d electron contribution to the momentum spectrum. Momentum spectra for Ag have been measured previously by the conventional single-detector Doppler-broadening technique[5–9] and by an angular-correlation technique.[10] These low-momentum spectra obtained from single-detector experiments have been used to deduce the monovacancy-formation enthalpies. These experiments were restricted to the temperatures ranging from 100 K to the melting point.[9]

The temperature dependence of those annihilations occurring with predominantly low-momentum electrons has been shown to be complicated, and no quantitative theoretical explanation has been produced. This is not too surprising as it involves the temperature dependence of both the positron and electron wave functions and the interaction of positrons with phonons and possibly with impurities and defects other than vacancies. In order to extract vacancy information from the low-momentum region it is therefore necessary to modify the two-state trapping model by including a prevacancy effect to account for the behavior of the momentum spectra before the onset of vacancy trapping. Therefore a semiempirical formula is employed to extract the vacancy-formation enthalpy. For a typical fcc metal, this prevacancy effect usually produces a change in slope as a function of temperature.[11] However, the Ag data available in the literature were not obtained at sufficiently low temperature to exhibit this effect. In this study, we show that Ag exhibits the same prevacancy effect in the low-momentum region as other fcc metals.

In a recent 2-D work,[3] the high-momentum results of Al were found to fit with the two-state trapping model used in extracting the vacancy-formation enthalpy. In this paper, we report 2-D spectra of Ag for a wide range of temperatures (9 to 1098 K) and show that these results provide further support for the applicability of this positron-annihilation technique in extracting defect information.

II. EXPERIMENTAL DETAILS

A sample of 99.999% pure polycrystalline Ag ($25.4 \times 25.4 \times 1$ mm thickness) was obtained from Metron Company. A 30-μCi ^{22}Na or a 15-μCi ^{68}Ge positron source was deposited as a thin film on one of the inside surfaces of a two-sample sandwich to minimize the source contribution to the annihilation photopeak. The samples were electron-beam welded together under vacuum (10^{-6} Torr) and subsequently annealed under 1-atm H_2 flow at 948 K for 24 h and also annealed *in situ* under high-purity Ar.

Two intrinsic Ge detectors with resolutions of 1.27 and 1.31 keV (full width at half maximum) at 10^4 counts per second were employed for all measurements. Low- and high-temperature measurements were made in He and high-purity Ar atmospheres, respectively. In both cases temperature deviations were less than ± 0.5 K. The electronics of the 2-D Doppler-broadening system were similar to those described elsewhere.[2]

The spectra were stored in a two-dimensional array, where the ordinate was the sum of the two annihilation photon energies, $E_T = E_1 + E_2$, and the abscissa was the difference between the energies of the same two photons, $\Delta E = E_2 - E_1$. Therefore, E_T reflects the binding of the electron and positron to the solid, and ΔE gives electron-momentum information due to the Doppler effect. The analyzed spectra were summed in E_T as a function of ΔE. E_T values were summed between $2m_0c^2 - 2.0$ keV and $2m_0c^2 + 0.8$ keV and ΔE values were measured from ± 18 keV about $\Delta E = 0$. At each temperature the summed momentum spectrum contained approximately 1 to 3×10^7 counts. These normalized spectra were analyzed in different regions, the first being a sum corresponding to the central region (S parameter), and the other two were summed over different high-momentum regions [$W(T), W'(T)$].

III. RESULTS AND DISCUSSION

Figures 1 and 2 show normalized peak parameters $S(T)$ and high-momentum components $W(T)$ from 9 to 1098 K, respectively. We have summed ΔE over ± 0.8 keV from the centroid of the peak to obtain the $S(T)$ values. This quantity is predominantly weighted by the conduction electrons, whereas the deep-core-electron contribution to this central region is small.[3] As shown in Fig. 1, the S parameter from the 2-D system is very similar to the single-detector spectra[5–9] from room temperature to 1098 K, though the 2-D system has a $\sqrt{2}$ better resolution than the single-detector system.[2] The low-temperature data below 400 K exhibit a slope that is much smaller than the slope between 400 and 650 K. This change of slope is similar to the typical temperature dependence of the line shape parameter for fcc metals indicated by Schulte *et al.*,[11] but not previously observed in Ag.

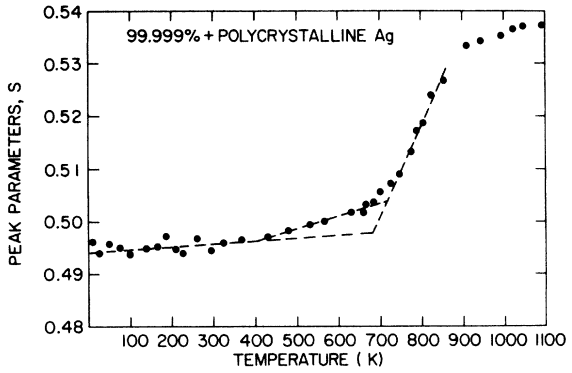

FIG. 1. $S(T)$ vs temperature (K) for 99.999% polycrystalline Ag. The peak parameter is summed in ΔE (± 0.8 keV) about $\Delta E = 0$ of 2-D Doppler-broadening spectra. The dashed lines are the result of fitting linear lines over three temperature regions for determining the onset temperatures, i.e., 682 and 722 K. The statistical error is about the size of the points on the plot.

The extraction of the vacancy-formation enthalpy from the S parameter has been widely discussed for various metallic systems.[12] The change of slope before observation of vacancy trapping in the S parameter is identified as a prevacancy region.[13,14] A

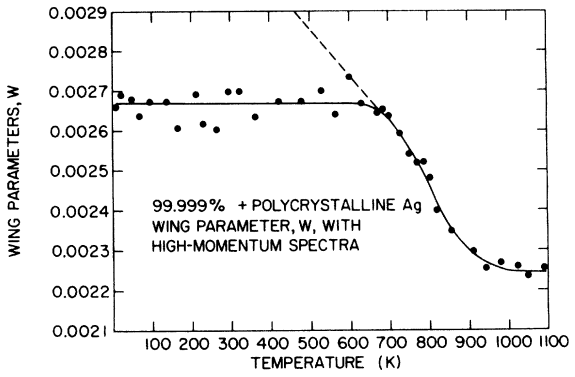

FIG. 2. $W(T)$ vs temperature (K) for 99.999% polycrystalline Ag. The high-momentum events are summed in ΔE between ± 6 and ± 18 keV about $\Delta E = 0$ in the 2-D Doppler-broadening spectra. Solid line is drawn as a guide to the eye. The onset temperature is 701 K. The dashed line is the theoretical result predicted by Stott and West (Ref. 19), where we extrapolated from 300 to 700 K. The low-temperature points are the result of two completely different runs which did not have the statistical accuracy of the high-temperature results, therefore exhibiting more scatter. The standard deviation is about 3 times the size of points on the plot for the low-temperature region but about the same size as the points for the high-temperature region.

number of different possibilites have been suggested[15] for this region but at the present time there is no accepted explanation. To extract quantitative information on the observed temperature dependence, it is necessary to know both the temperature dependence of the positron and electron wave functions and how they couple to the lattice.

However, by using the high-momentum part of the spectrum, we find a simple temperature dependence as shown in Fig. 2. In this case, we chose the integration of high-momentum components to be

$$\int_{-18}^{-6} P(\Delta E)d(\Delta E) + \int_{6}^{18} P(\Delta E)d(\Delta E) \ ,$$

where $P(\Delta E)$ is the probability that the annihilation of the positron results in the emission of two photons where the energy difference ΔE lies within the specified integration limits (given in keV). This quantity $W(T)$ is essentially flat before 650 K, after which dramatic changes indicate the onset of positron trapping at thermally generated vacancies. The effect of vacancies is observed between 650 and 980 K, saturating at the higher temperatures. This behavior permits the direct application of the two-state trapping model[12] in extracting the vacancy-formation enthalpy E_F, using the following:

$$-E_F/k_B T = \ln(A) + \ln\frac{I(T)-I(0)}{I(\infty)-I(T)} \ , \qquad (1)$$

where k_B is the Boltzmann constant, T is the temperature in K, $I(T)$, $I(0)$, and $I(\infty)$ are the wing components at temperature T, at 0% trapping (low T) and at 100% trapping (high T), respectively. The quantity A is determined by the product of the perfect-lattice positron lifetime, the specific trapping rate, and the expression of $\exp(S_F/k_B)$, where S_F is the formation entropy.[3] Here $I(0)$ and $I(\infty)$ are better defined numbers than those obtained using the S parameter, because $W(T)$ is essentially flat at sufficiently low and high temperatures. Small errors in these two limits $[I(0), I(\infty)]$ can seriously affect the extraction of the vacancy-formation enthalpy.

From the slope of the plot of $\ln\{[I(T)-I(0)]/[I(\infty)-I(T)]\}$ vs $1/T$ in Fig. 3, we obtain a value of 1.11 ± 0.05 eV for E_F. This value is within the limits of the reported values[12] for Ag ranging from 0.99 to 1.20 eV. The Arrhenius plot of $W(T)$ shows that the two-state trapping model provides a good representation of this system. The method of determining the vacancy-formation enthalpies through the use of high-momentum components appears to be the most reliable available, as one can observe the linearity of the Arrhenius plot over several orders of magnitude. Even with this procedure one should realize that data points at the onset or near saturation can produce systematic errors in the extraction of a reliable value for the vacancy-formation enthalpy. This degree of sensitivity or direct applicability has not been found using the S parameter or mean-lifetime measurements in most fcc metals.

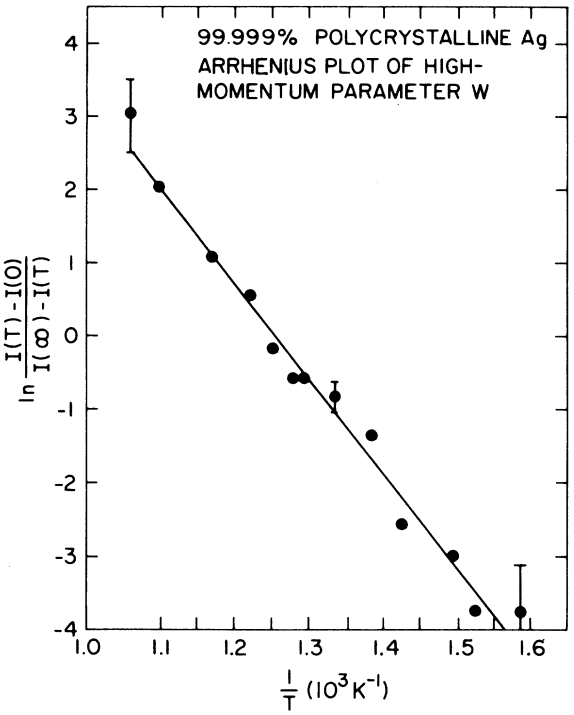

FIG. 3. Arrhenius plot of $\ln\{[I(T)-I(0)]/[I(\infty)-I(T)]\}$ vs $1/T$ of 99.999% polycrystalline Ag from Eq. (1). $I(\infty)$ and $I(0)$ are the assumed 100% and 0% trapping. $I(\infty)$ and $I(0)$ are taken from high-momentum spectra of Fig. 2 which are 0.002 24 and 0.002 67, respectively.

The changes observed in the mean positron lifetime and the S parameter when positron trapping occurs are dominated by the conduction electrons whereas the high-momentum tails represent only those annihilations with deep-core electrons. The core electrons do play a small part in determining the positron lifetime. The temperature dependence of the mean lifetime and Doppler-broadening parameter $S(T)$ may not be the same, although for Ag they do exhibit a similar dependence,[5–9,16] where both the mean lifetime and the S parameter exhibit a change of slope before trapping of positrons at vacancies is observed. As mentioned, $W(T)$ is derived mainly from core-electron annihilations and does not show the same temperature dependence before the onset of positron trapping at vacancies as either the S parameter or the mean lifetime. In their use for the determination of the vacancy-formation enthalpy, lifetime measurements require a sophisticated computational method in order to deduce the annihilation rates correctly, and in many cases the fitting parameters are strongly correlated and the true values cannot

be unambiguously extracted.

Quantitative self-consistent band calculations of the annihilation characteristics between the conduction electrons are complicated and have not been performed. These already-difficult calculations are complicated by the large enhancements above the predictions of the independent-particle model[12] (IPM) arising from the correlations between the positron and the electron under consideration.[3] On the other hand, recent IPM calculations[3,17] in Al and Cu show excellent agreement between theory and experiment in both the shape and absolute intensity of the high-momentum spectra in the perfect crystals. It has been shown theoretically[17] that the deeply bound core electrons are only slightly perturbed by positrons and the simple IPM calculations suffice to describe the high-momentum spectra. The only measurable change in the core spectra as a function of temperature appears when positron trapping at vacancies occurs.

The main problem in utilizing the high-momentum region of the spectrum is poor statistics. It is therefore necessary to collect the spectrum over a longer time period compared with the single-detector Doppler-broadening system in order to obtain good statistical accuracy. In principle, the same accuracy can be achieved with the high-momentum region relative to the peak parameter with less statistics because the high-momentum part produces a larger fractional change when trapping occurs. In the central region it is not sufficient to have a high degree of accuracy in the measurements because even small temperature-dependent effects, not accounted for by the simple trapping model, lead to significant changes in the relevant quantities. This could prohibit the investigation of an otherwise sound model. Furthermore, for the higher-momentum component the simple IPM can describe the perfect-crystal results; therefore, quantitative calculations can be made for the vacancy case.

In order to select the integration region for the wing component $W(T)$, we plot the ratio of momentum spectra between three temperatures (428, 723, and 943 K) and 293 K as a function of ΔE in Fig. 4. At high temperatures where positron trapping at vacancies is close to saturation, we observe positrons annihilating with a higher probability with low-momentum electrons than with high-momentum electrons. Therefore, as expected the ratios near the centroid are greater than 1, but are significantly less than one in the higher-momentum region. A noteworthy feature in the ratio curve is the second peak at 5.5 keV. This value does not correspond to the Fermi momentum of the conduction electron of Ag, for which ΔE is approximately 2.3 keV (assuming perfect resolution). The actual electron-momentum spectra are convoluted with an effective-detector-resolution function ($\sim$1 keV); therefore,

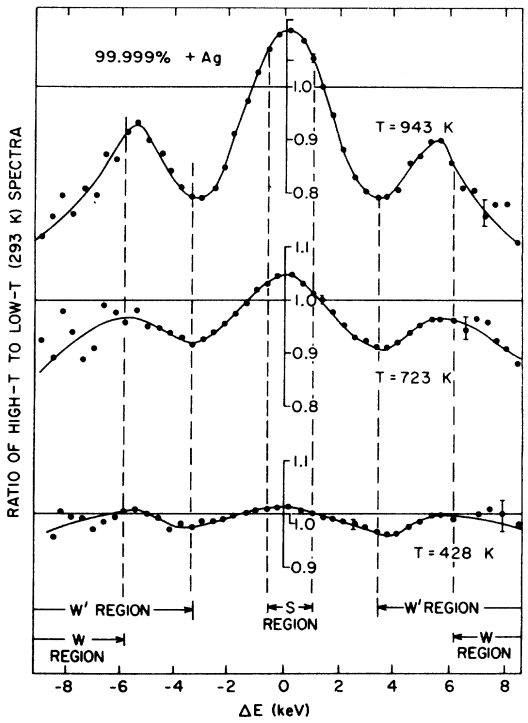

FIG. 4. Doppler-broadening-spectra ratio between high and low temperatures (293 K). Each spectrum is normalized to 1 in the total events before the ratio is taken.

the extraction of the correct momentum spectrum for this low-momentum region requires deconvolution, whereas the high-momentum region is essentially independent of detector resolution. Furthermore, these ratio curves do not show a positron localization bump[18] at the Fermi surface, as does[3] Al because of the smearing of the Fermi momentum by the d electrons in Ag. The second peak which we associate mainly with the d electrons starts to appear even before vacancy trapping is detected in $W(T)$ or $S(T)$. A more thorough investigation of this phenomena will be reported in a later paper, although we attribute this effect to the narrowing of the d-electron momentum distribution. At present we will show that including this second peak in the integration region seriously affects the determination of the vacancy formation enthalpy.

If the second peak (Fig. 4) is included in $W(T)$,

$$\int_{-18}^{-3.2} P(\Delta E)d(\Delta E) + \int_{3.2}^{18} P(\Delta E)d(\Delta E) \ ,$$

with the integration limits given in keV, we find the curve $W'(T)$ shown in Fig. 5. Comparing Fig. 5 with Fig. 2, a large difference is found in the curves, especially in the temperature range before vacancy trapping. There is a single slope between 9 and 750 K which is different from either of the two slopes in the S parameter (Fig. 1), and also different from the ap-

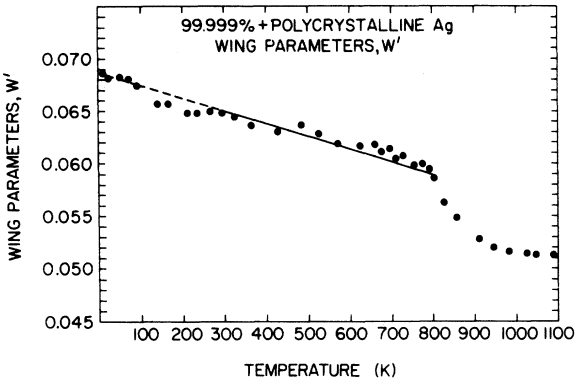

FIG. 5. $W'(T)$ vs temperature (K) for 99.999% polycrystalline Ag. The $W'(T)$ region is summed in ΔE between ± 3.2 and ± 18 keV about $\Delta E = 0$ in the 2-D Doppler-broadening spectra. The solid line is derived from the theoretically calculated change in core annihilation rate from Stott and West (Ref. 19) between 300 and 800 K. The dashed line is the extracted theoretical prediction to 9 K. The statistical standard deviation is about the size of points shown. The onset temperature is 800 K.

proximately zero slope of $W(T)$ (Fig. 2). The Arrhenius plot of $W'(T)$ from Fig. 5 does not show a simple straight line as in Fig. 3, and the extraction of a vacancy-formation enthalpy is very difficult. These results suggest that only high-momentum events ($\Delta E > 5.5$ keV), corresponding to $W(T)$, are suitable for providing a reliable vacancy formation enthalpy in this case. We have no reason to expect Ag to be anomalous in this respect; therefore we expect this to be a general phenomenon, at least in the noble metals.

Using the pseudopotential method, Stott and West[19] calculated a 16% change in the core annihilation rate from 300 to 800 K. Previous results[20] in Al and the high-momentum spectra in Ag of this work both show negligible annihilation-rate changes before the onset of vacancy trapping contrary to their findings. Large changes in the region below the onset of vacancy trapping are observed in Fig. 5, when we include the second-peak contribution in the integration region [$W'(T)$]. The theoretical prediction of Stott and West is shown in the dashed line in Fig. 5. We find good agreement with their calculation even from 9 to 300 K when compared to $W'(T)$, which is thought to be fortuitous. The annihilation characteristics of those positrons annihilating with the deeply bound core electrons do not appear to respond to lattice expansion and lattice vibrations. Those positrons annihilating with low-momentum and conduction electrons show a large temperature effect before the region of trapping at vacancies.

Lastly, it is worthwhile to mention that the vacancy-formation enthalpy determined by the threshold-temperature method[12] using the three figures (Figs. 1, 2, and 5) shows serious differences. The threshold temperatures obtained by linear fitting over two temperature regions are ~ 722 K from the $S(T)$ curve (Fig. 1), ~ 701 K from the $W(T)$ curve (Fig. 2), and ~ 800 K from the $W'(T)$ curve (Fig. 5). The resulting E_F values obtained by these threshold temperatures differ by approximately 0.14 eV. We conclude that one should be very careful in comparing results obtained from this method as they are dependent on the region of integration in ΔE.

In conclusion, we find that the high-momentum component, $W(T)$, is the most reliable method for determining vacancy formation enthalpies. The vacancy formation enthalpy of Ag is found to be 1.11 ± 0.05 eV by analyzing the high-momentum components. In Ag the high-momentum events do not appear to respond to thermal expansion as do the mean-lifetime and S parameter, but they change significantly when vacancy trapping occurs. A second peak was observed at ~ 5.5-keV Doppler shift in the ratio curves between the high- and low-temperature momentum spectra. This second peak does not correspond to the zero-point motion of the localized positron but is thought to be associated with the temperature dependence of the positron's interaction with $4d$ electrons. This peak appears in the ratio curves before the onset of positron trapping at vacancies is detected. In applying the Doppler-broadening or angular-correlation method, one should be careful to choose the region of integration that begins beyond the second peak which appears in the ratio curves in order to extract an accurate vacancy formation enthalpy.

ACKNOWLEDGMENTS

We are grateful to A. N. Goland for his continuous support and reading this manuscript, to P. Schultz for his assistance is setting up a computer program for analyzing 2-D spectra, to J. Hurst for his technical assistance, and to D. O. Welch, I. K. MacKenzie, and C. L. Snead, Jr., for valuable discussions. This work is supported by the Department of Energy under Contract No. EY-76-C-02-0016.

*Present address: Texas Instruments, Houston, Tex.
[1]For example, see a review by R. N. West in Adv. Phys. 22, 263 (1973).
[2]J. R. MacDonald, K. G. Lynn, R. A. Boie, and M. F. Robbins, Nucl. Instrum. Methods 153, 189 (1978).
[3]K. G. Lynn, J. E. Dickman, W. L. Brown, M. F. Robbins, and E. Bonderup, Phys. Rev. B 20, 3566 (1979).
[4]E. Bonderup, J. U. Anderson, and D. N. Lowy, Phys. Rev. B 20, 883 (1979).
[5]J. L. Campbell, Appl. Phys. 13, 365 (1977).
[6]J. L. Campbell, C. W. Schulte, and J. A. Jackman, J. Phys. F 7, 1985 (1977).
[7]J. L. Campbell, C. W. Schulte, and R. R. Gingerich, J. Nucl. Mater. 69-70, 609 (1978).
[8]W. Triftshäuser and J. D. McGervey, Appl. Phys. 6, 177 (1975).
[9]P. C. Lichtenberger, Ph. D. thesis (University of Waterloo, Canada, 1974) (unpublished).
[10]E. H. Becker, A. G. Gould, E. M. Senicki, and B. G. Hogg, Can. J. Phys. 52, 336 (1974).
[11]C. W. Schulte, J. L. Campbell, and J. A. Jackman, Appl. Phys. 16, 29 (1978).
[12]For example, see a recent review book edited by P. Hautojärvi, *Positrons in Solids* (Springer, Heidelberg, 1979).
[13]I. K. Mackenzie and P. C. Lichtenberger, Appl. Phys. 9, 331 (1976).
[14]A. Seeger, Appl. Phys. 7, 85 (1975).
[15]P. Schultz. M. S. thesis (Guelph University, Canada, 1978) (unpublished).
[16]B. T. A. McKee and T. McMullen, J. Phys. F 8, 1175 (1978).
[17]K. G. Lynn, J. R. MacDonald, R. A. Boie, L. C. Feldman, J. D. Gabbe, M. F. Robbins, E. Bonderup, and J. Golvchenko, Phys. Rev. Lett. 38, 241 (1977).
[18]M. A. Shulman and S. Berko, Proceedings of the Fourth International Conference Positron Annihilation, Helsinger, Denmark, E31, 1976 (unpublished).
[19]M. J. Stott and R. N. West, J. Phys. F 8, 635 (1978).
[20]J. E. Dickman and K. G. Lynn, J. Phys. F 8, L295 (1978).