Pressure dependence of the angular correlation of positron-annihilation radiation in sodium

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The pressure dependence of the angular correlation of positron-annihilation radiation in sodium was measured in the range from 4 to 68 kbar. Below 55 kbar the measured value of θ_F was consistent with the predictions of the nearly-free-electron model. Above 55 kbar, θ_F deviated from the nearly-free-electron model, indicating that above 55 kbar the electronic structure of sodium metal may no longer be free-electron-like. The percentage of core annihilations varied smoothly from 30% at 4 kbar to 42% at 68 kbar. As pointed out by Kubica and Stott, this increase in the core-annihilation percentage with pressure allows the measurements of the pressure dependence of the positron lifetime in sodium made by MacKenzie, LeBlanc, and McKee to be explained. The pressure dependence of the enhancement of the electrons at the positron was also examined. Reasonable absolute agreement with the theories of Kahana and Carbotte was observed, but the variation in the ratios of the enhancement coefficients with pressure was not in agreement with the theoretical predictions.

I. INTRODUCTION

Sodium metal has several attributes which make it attractive for a study of the pressure dependence of the positron-annihilation characteristics: It is highly compressible,[1] thus large changes of the electron density can be achieved with moderate pressure. The low-pressure valence electron structure is nearly free-electron-like with a Fermi surface which is nearly spherical.[2-4] The ion cores are much smaller than the interatomic separation resulting in a reasonably small core electron contribution to the annihilation characteristics and in a core electron structure which does not change significantly over the pressure range used in this work.

MacKenzie, LeBlanc, and McKee[5] have measured the effect of pressure on the positron annihilation rate in sodium and the other alkali metals. They observed that the annihilation rate was both somewhat larger and varied more rapidly than predicted for annihilation with valence electrons alone.[6] These results, by themselves, were not disturbing; they could be explained by including the core contribution. Qualitatively, the argument is simply that the increase in the zero pressure result over the valence-electron prediction is the result of annihilation with core electrons. The increased variation of the annihilation rate with pressure is due to increased positron penetration into the cores as the material is compressed, thus increasing the core annihilation rate more rapidly than the valence annihilation rate. Recently Kubica and Stott[7] have made quantitative calculations of the core contribution as a function of pressure and found that the results of MacKenzie *et al.* could indeed be explained on this basis. However, MacKenzie *et al.* had made an additional measurement which was at variance with this interpretation. They had also measured the Doppler broadening of the annihilation radiation spectrum as a function of pressure using a Ge(Li) spectrometer. This measurement yields the momentum distribution of the annihilating electron-positron pairs and can be deconvoluted to yield the percentage of core annihilation, albeit with only a very limited resolution. They observed no change in the percentage of core annihilation with pressure. If this were indeed true, the theories of positron annihilation would be in need of serious revision. Of course, it was also possible that the change in the core annihilation percentage was not observed because of the inherently poor resolution of the Ge(Li) spectrometer method. For this reason it was felt that high-resolution angular correlation measurements of the pressure dependence of the momentum distribution should be made. Such measurements would provide an accurate measurement of the variation of the core contribution as a function of pressure and thereby resolve the problem raised by the measurements of MacKenzie *et al.* In addition, angular correlation measurements would also yield values for the variation of the electron enhancement at the positron as a function of electron density and provide information on the electronic structure of sodium metal at high pressures.

II. EXPERIMENTAL PROCEDURE

The sample consisted of two discs of high-purity sodium metal, each 6 mm in diameter and 0.25 mm thick. The sodium metal was obtained from the MSA Research Corp. The positron source consisted of 30 mCi of Cobalt-58 plated on a 6-μm copper foil. The source was sandwiched between

the two disks of sodium. Preparation of the sample was carried out in an inert gas atmosphere and the sample-source assembly was immediately pressurized to 4 kbar to seal it against atmospheric deterioration. The necessity of sealing the sample from the atmosphere prevented measurement at zero pressure. The samples were pressurized in a Bridgman opposed-anvil high-pressure cell described previously.[8] The pressure cell was calibrated using the resistance discontinuities of bismuth which occur at 25, 28, and 76 kbar.[9]

The angular correlations were measured with conventional long-slit apparatus with a geometrical resolution of 0.5 mrad. Measurements were made over the pressure range from 4 to 68 kbar.

The unavoidable use of an internal positron source in high-pressure positron studies results in a significant fraction of the positrons annihilating in the copper source foil instead of in the sodium sample. The percentage of annihilations occurring in the source foil was estimated by finding the linear combination of a pure sodium angular correlation[10] and a pure copper angular correlation[11] which best fit the angular correlation measured at 4 kbar. The result was that it was estimated that $18 \pm 4\%$ of the positrons annihilated in the copper source foil. All the measured angular correlations were corrected for source foil annihilations by subtracting a pure copper angular correlation which had an area equal to 18% of the total area of the measured angular correlation. No correction was made for the compression of the copper foil since copper is not highly compressible; the density of copper at 45 kbar is only 3% greater than the zero pressure density.[12] The error in the estimate of the source percentage was the largest single source of error in the experiment. In all cases this systematic error was as large or larger than the statistical errors. The error bars shown in the various figures include the systematic source foil error. This is why the error bars in most of the cases are far larger than the apparent statistical variation of the data points.

III. RESULTS AND DISCUSSION

A. Data analysis

The angular correlation from sodium has two basic components: (i) the narrow central peak, which is approximately parabolic in shape, which results from annihilation with valence electrons, and (ii) the wide, so-called, core component which is nearly Gaussian in shape. The core component is due primarily to annihilations with the electrons in the inert gas core of the sodium atoms, but a portion of the core component is due to higher momentum components of the valence electrons. In sodium this portion is not large and the results, with one exception, are not affected significantly. The exception is that the measured core percentage includes the higher momentum components of the valence electrons and, therefore, the measured core percentage is expected to be slightly larger than theoretical estimates of the core percentage. However, the amount of the overestimate should be nearly independent of the pressure as long as the valence electron structure is nearly-free-electron-like.

If one assumes that the Fermi surface of sodium is nearly spherical and that the enhancement of the electron density at the positron $\epsilon(\gamma)$ has a momentum dependence of the form calculated by Kahana,[13]

$$\epsilon(\gamma) = a + b\gamma^2 + c\gamma^4 , \tag{1}$$

where γ is the reduced electron momentum, $\gamma = (p/p_F)$, then the valence electron component of the angular correlation $N_v(\theta)$ will be

$$N_v(\theta) = A[(\tfrac{1}{2}a + \tfrac{1}{4}b + \tfrac{1}{6}c) - \tfrac{1}{2}a(\theta/\theta_F)^2 - \tfrac{1}{4}b(\theta/\theta_F)^4 - \tfrac{1}{6}c(\theta/\theta_F)^6] . \tag{2}$$

A is the normalization factor and $(\theta/\theta_F) = \gamma$, since $\theta = p/mc$. The experiment of Donaghy and Stewart[4] has shown that a momentum-dependent enhancement term is needed to explain the angular correlation of sodium and that the form in Eq. (2) fits the observed zero-pressure valence-electron component.

It is empirically clear that the core component in sodium is very close to Gaussian in shape beyond θ_F. Since theoretical estimates[14] of the sodium core component for $\theta < \theta_F$ do not deviate significantly from a Gaussian shape either, the core component $N_c(\theta)$ was approximated by the Gaussian

$$N_c(\theta) = B \exp(-\theta^2/\theta_G^2) . \tag{3}$$

The total angular correlation $N(\theta)$ can be represented by

$$N(\theta) = N_v(\theta) + N_c(\theta) . \tag{4}$$

However, Eq. (4) does not include the effect of experimental resolution. This was taken into account by convoluting $N(\theta)$ with a triangular resolution function with a half-width of 0.8 mrad. This resolution function is not exact, but it adequately approximates the convolution of the triangular geometrical resolution and the broadening caused by the thermal motion of the position.[15]

A least-squares fit of the function $N(\theta)$, convoluted with the experimental resolution, was made to the measured angular correlations. The six fitting parameters were Aa, Ab, Ac, B, θ_F, and

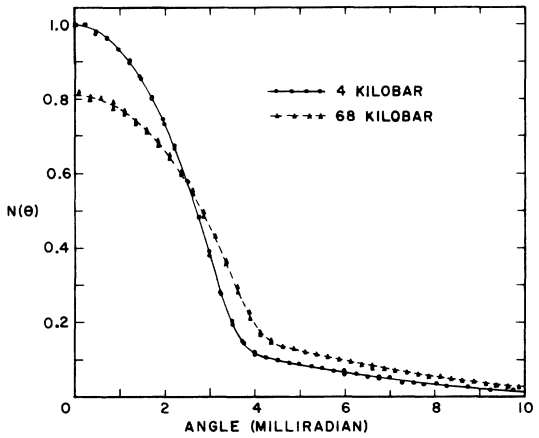

FIG. 1. Angular correlation of positron-annihilation radiation from sodium at 4 and 68 kbar. The lines are the least-squares fit of $N(\theta)$. The source foil background has been subtracted.

θ_G. The fit was consistent with the measurements in all cases. Representative results for 4 and 68 kbar are shown in Fig. 1. The values of the fitting parameters are given in Table I.

The errors caused by the uncertainty in the estimate of the fraction of annihilations occurring in the source foil were estimated by fitting representative angular correlations using source foil annihilation percentages of 14 and 22%.

B. Valence-electron structure

The measured values of θ_F as a function of pressure are shown in Fig. 2. Also shown is the variation of θ_F with pressure predicted for a free-electron gas with a spherical Fermi surface. For pressures below 45 kbar, the calculation of the free-electron value of θ_F was made using the measurements of the volume of sodium as a function of pressure made by Vaidya, Getting, and Kennedy.[1] For pressures above 45 kbar, the compressibility measurements of Bridgman[16] were used.

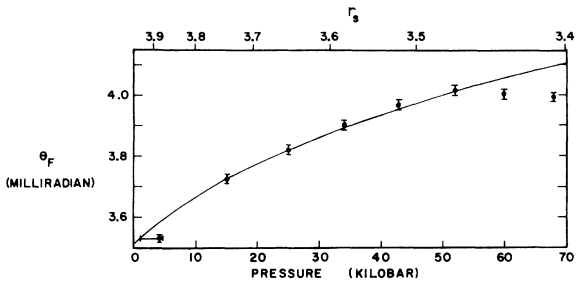

FIG. 2. Variation of θ_F with pressure. The line is the variation predicted by the free-electron model.

The pressure scale of Bridgman's results was adjusted to a bismuth III-V transition pressure of 76 kbar instead of Bridgman's original value of 88 kbar.[17] When this was done, only a very slight adjustment in Bridgman's result was needed to connect it smoothly to the results of Vaidya *et al.*

Below 55 kbar the measured values of θ_F are in complete agreement with the free-electron-model prediction. The slight deviation of the nominal 4-kbar point is most likely the result of the actual pressure in the cell being considerably less than 4 kbar, an event which occurs more often than not with Bridgman-type high-pressure cells in the range below 10 kbar. Below 10 kbar the gasket often carries a disproportionate, but unreproducible, share of the press load, thus reducing the actual pressure in the sample below the nominal value.

Above 55 kbar the measured value of θ_F deviates significantly from the free-electron prediction. This indicates that above 55 kbar the electronic structure of sodium metal may start to deviate from nearly-free-electron-like. This hypothesis is consistent with the high-pressure behavior of the resistivity of sodium which starts to increase significantly in the same pressure range.[18] It would be fruitless to speculate about the fundamental cause of the observed deviation with only the

TABLE I. Parameters used to fit observed angular correlations.

Pressure (kbar)	Aa	Ab	Ac	θ_F (mrad)	B	θ_G (mrad)
4	0.495	0.0809	0.0903	3.53	0.0536	6.42
15	0.436	0.0869	0.0826	3.73	0.0573	6.72
25	0.402	0.0918	0.0814	3.83	0.0600	6.79
34	0.380	0.0980	0.0781	3.90	0.0614	6.90
43	0.360	0.1006	0.0756	3.96	0.0626	7.03
52	0.348	0.1034	0.0746	4.01	0.0631	7.12
60	0.341	0.1049	0.0738	4.00	0.0649	7.07
68	0.330	0.1045	0.0694	3.99	0.0693	6.94

present results, the variation of the resistivity, and the few other bits of information that are available concerning the high-pressure behavior of sodium metal. Distortion of the Fermi surface, many-body effects, mixing of the valence states with other states, and other things are possibilities. The effects of several of these on the angular correlation were calculated and it was found that most of them could produce a deviation of the type observed. Unless a way was found to measure the angular correlation at high pressures using single-crystal samples of sodium, it is unlikely that the angular correlation method could be used to distinguish among the various possibilities.

C. Core fraction

The percentage of annihilations taking place with the core electrons was estimated by comparing the area of the fitted Gaussian with the total area of the angular correlation. This, of course, overestimates the actual core fraction slightly since the Gaussian part also contains a small portion due to higher momentum components of the valence electrons. The percentage of core annihilations as a function of pressure is shown in Fig. 3. The percentage of core annihilations varies from 30% at 4 kbar to 42% at 68 kbar with an uncertainty of ±2%. As pointed out by Kubica and Stott,[7] this change in the core percentage with pressure explains the pressure dependence of the positron lifetime in sodium observed by MacKenzie *et al.*[5] Kubica and Stott have calculated that the core percentage should be 25% at 15 kbar and 32% at 75 kbar. These values are slightly smaller than the measured values but this is not surprising since the measured core percentages include a substantial contribution from high-momentum valence-electron components.

The width of the fitted Gaussian as a function of pressure is shown in Fig. 4. The gradual increase in width below 55 kbar is probably the result of increased positron penetration into the atom core

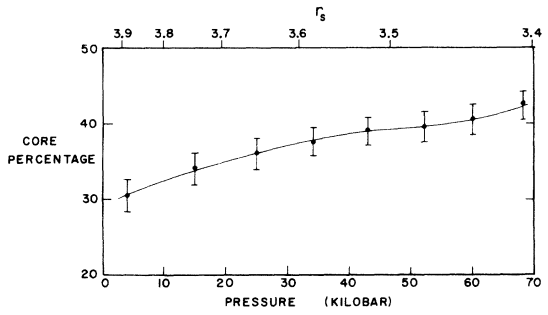

FIG. 3. Percentage of core annihilations as a function of pressure. The line is a visual fit.

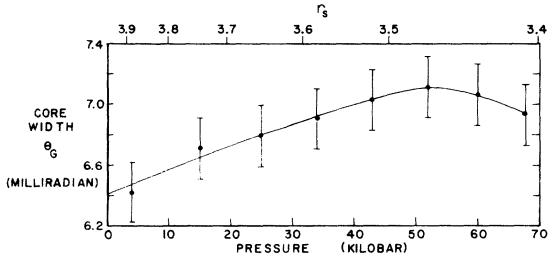

FIG. 4. Pressure dependence of the width (θ_G) of the least-squares Gaussian fit to the core component of the angular correlation from sodium. The line is a visual fit.

as the sodium is compressed. As Kubica and Stott's[7] calculation of the positron wave function in compressed sodium shows, the positron wave function increases most rapidly in the central region of the core as the sodium is compressed. This results in an increase in the percentage of annihilations occurring with the high-momentum electrons in the inner atomic core, thus producing a broadening of the core component of the angular correlation. The rather abrupt narrowing of the core component above 55 kbar is consistent with the previously discussed deviation of θ_F from the free-electron prediction. As the valence-electron structure, for whatever reason, deviates from nearly-free-electron-like, the percentage of higher-momentum components would increase, with the most rapid increase occurring in the region just beyond θ_F, thus resulting in a narrowing of the so-called core contribution. This would also result in a small increase in the area of the Gaussian part beyond that expected, due to increased penetration of the positron into the core. Indeed a slight upturn in the core fraction does seem to occur in the region above 55 kbar.

D. Enhancement

The values of the individual enhancement coefficients, a, b, and c, cannot be measured with the angular correlation method because the shape of the angular correlation is independent of the total annihilation rate; i.e., the normalization coefficient A is unknown. Only the ratios of the enhancement coefficients, such as b/a and c/a, can be extracted from the results. There is also a further difficulty in that the exact shape of the core contribution in the region $\theta < \theta_F$ is unknown and the values of the extracted ratios are sensitive to the choice of the approximation used for the core contribution. The measured values of b/a and c/a for sodium are shown in Fig. 5. The values are plotted against r_s, the radius of a sphere containing

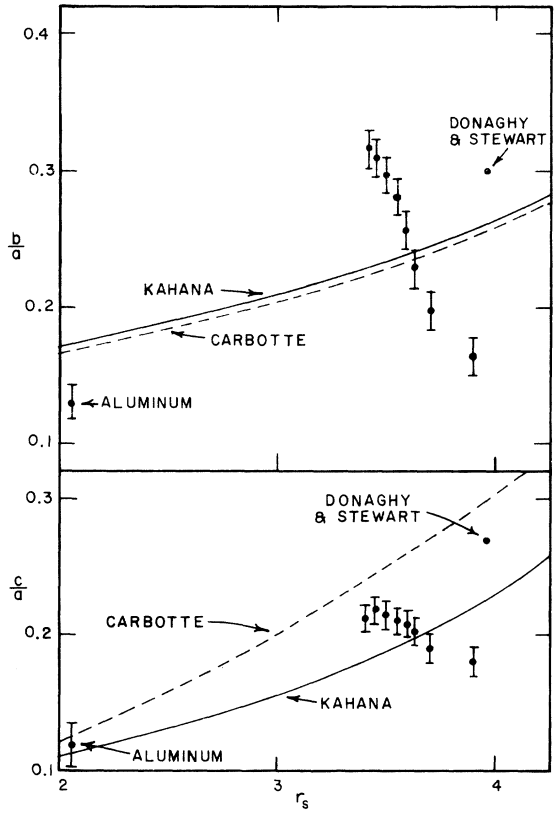

FIG. 5. Ratios of the enhancement coefficients, b/a and c/a, in sodium as a function of electron density. r_s is in atomic units. Also shown are the theoretical predictions of Kahana (Ref. 13) and Carbotte (Ref. 19), the zero pressure values for sodium measured by Donaghy and Stewart (Ref. 4), and the values measured in aluminum at zero pressure.

one valence electron on the average. The values of r_s were calculated using the same pressure dependence of the volume as used in Sec. III B. Also shown in Fig. 5 are the values of b/a and c/a predicted by Kahana[13] and the more recent predictions of Carbotte.[19] The values measured by Donaghy and Stewart[4] for sodium at zero pressure are given, as are the values measured for an annealed aluminum sample. The aluminum angular correlation was measured using an external positron source and the ratios were extracted using the same fitting procedures as were used for sodium. Considering the magnitude of the error that uncertainties in the core approximation might introduce, the results are in reasonable absolute agreement with the theoretical predictions. The source of the discrepancy between the results of Donaghy and Stewart and the present results could not be determined. It did not appear to be the difference in the core approximation used. The b/a and c/a ratios were also computed using a MgO angular correlation[20] to approximate the core component, as Donaghy and Stewart did. The results were the same, within experimental error, as those calculated using the Gaussian core approximation.

The slopes of the experimentally measured ratios of the enhancement coefficients versus r_s are obviously in disagreement with the theoretical predictions and this disagreement remains unexplained. The discrepancy does not appear to be due to the systematic error caused by the source foil correction; as mentioned, the error bars include this error. Nor does it seem likely that the core correction uncertainty could cause such a large error. The core percentage only changes from 30 to 42% over the pressure range used and no large change in the core shape is expected or observed. While the results shown in Fig. 5 were calculated with the core width varying as shown in Fig. 4, the enhancement ratios were also extracted using fixed width core component approximations. One approximation was a Gaussian fixed at the 4 kbar width, the other was the MgO angular correlation.[20] These approximations yielded the same enhancement ratio, within experimental error, as the variable width Gaussian approximation did. The possibility of the discrepancy being caused by the fitting procedure can be ruled out by the following considerations: There are four features of the angular correlations which are quite distinct with very sharp chi-squared minima. These are the maximum height of the curve θ_F and the two Gaussian parameters. If the Gaussian is subtracted and the peak height and θ_F are normalized, the valence electron contribution will be

$$(1-\gamma^2)+b[\tfrac{1}{4}(\gamma^2-\gamma^4)]+c[\tfrac{1}{6}(\gamma^2-\gamma^6)], \qquad (5)$$

where $\gamma = k/k_F = \theta/\theta_F$. Over the range of interest from $\gamma = 0$ to $\gamma = 1$, $\frac{1}{4}(\gamma^2-\gamma^4)$ and $\frac{1}{6}(\gamma^2-\gamma^6)$ are not too different in either shape or value. Thus the fitted values of b and c are subject to some error; however, the errors will be compensating to preserve the fit because both the b and c terms are positive. That is, $(b+c)$ will be essentially constant. We can see from Fig. 5 that if some change in the fitting procedure were to improve the fit of the measured values of b/a to the theoretical curve, the fit of c/a would become worse and vice versa. Therefore the fundamental discrepancy between the measured and theoretical values is not likely to be an artifact of the fitting procedure.

The measured and predicted enhancement coeffi-

cient ratios for aluminum, which also has a nearly spherical Fermi surface, are in close agreement. This rules out the possibility that the trend observed in sodium could be a simple consequence of the change in electron density.

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