by 2, are presented in Table III, together with the corresponding experimental values. The agreement is poor. It is seen that as one proceeds from the total ionization cross section to the doubly differential cross section, the agreement with experiment becomes poorer.

Because of the meagerness of Born approximation results the comparison with experimental results is very sketchy. A need is clearly shown for more extensive calculations, as well as a need for experimental measurements at higher proton energies where the Born approximation is expected to be valid and deviations could be attributed to the treatment of the hydrogen molecule as equivalent to two hydrogen atoms.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Charles J. Cook for designing and testing some of the apparatus used in this experiment and for his continued interest in the problem. We wish to thank W. Lang for expert accelerator operation, F. J. Sazama for assisting with the reduction of data, Eugene Rudd and D. E. McArthur for the computation of the Born approximation calculation, L. H. Sohl for construction and testing of the magnetometer, and A. Maschke for stimulating discussions. The expert assistance of J. S. Heiser and D. J. Fuehring in construction of the apparatus is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 130, NUMBER 4 15 MAY 1963

Positron Annihilation in Liquid and Solid Mercury*

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Results are presented of a study of the angular correlation of photons from the annihilation of positrons with electrons in solid and liquid mercury. The angular distribution of photon coincidences can be separated into contributions arising from annihilations with the ionic-core electrons and with the conduction electrons. The angular variation of the former does not appear to change at the solid-liquid transition, but the distribution for the conduction electrons is considerably modified. The plot of the number of coincidences against angle for the conduction electrons in the solid can be fitted very well by a parabola corresponding to two free electrons per atom, which indicates that the Fermi surface in extended k space does not depart very significantly from a sphere. The relative number of annihilations from the conduction electrons in the liquid is considerably greater and the distribution departs from the free electron parabola at large angles. These effects are interpreted in terms of the distortion of the wave functions and the broadening of the electronic energy levels by the disorder in the liquid. It is concluded that the uncertainty in the wave vector of an electron at the Fermi surface in the liquid is about 20% of the Fermi wave vector.

INTRODUCTION

THE electronic band structure of liquid metals has recently been the subject of considerable theoretical and experimental investigation. On the one hand, an attempt has been made to calculate the electronic eigenfunctions and energy levels,[1,2] and on the other a number of measurements of the optical[3] and transport properties of liquid metals[4] have been made to determine experimentally some features of the electronic band structure and scattering mechanisms. Because of their inherent nature as disordered structures, the electronic free path in liquid metals is short and it is not therefore feasible to carry out such experiments as the de Haas–van Alphen or magnetoacoustic effects, which have been successfully applied to the determination of the Fermi surface in solid metals. This limitation does not apply to the study of the angular correlation of the photons created when positrons annihilate with the electrons in a metal however, and valuable information can be obtained from such measurements.[5]

The purpose of the experiments described in this paper was to make a comparison of the electronic structures of mercury in the solid and liquid states by comparing the photon distribution from the two phases. A study of positron annihilation in liquid mercury has previously been made by Stewart,[6] but he did not compare the angular distribution with that for the solid and so was unable to draw any explicit conclusions about the electronic structure of the liquid. In this work the distribution of angular correlations was obtained both for the liquid and the solid phases and it has proved possible to deduce from the results a number of con-

* Contribution No. 1257. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1] S. F. Edwards, Proc. Roy. Soc. (London) **A267**, 518 (1962).

[2] V. Heine, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 279.

[3] L. G. Schulz, Advan. Phys. **6**, 102 (1957); J. N. Hodgson, Phil. Mag. **6**, 509 (1961).

[4] C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. **7**, 865 (1962).

[5] A. R. Mackintosh, U. S. Atomic Energy Commission Report IS-299 (1962).

[6] A. T. Stewart, Can. J. Phys. **35**, 168 (1957).

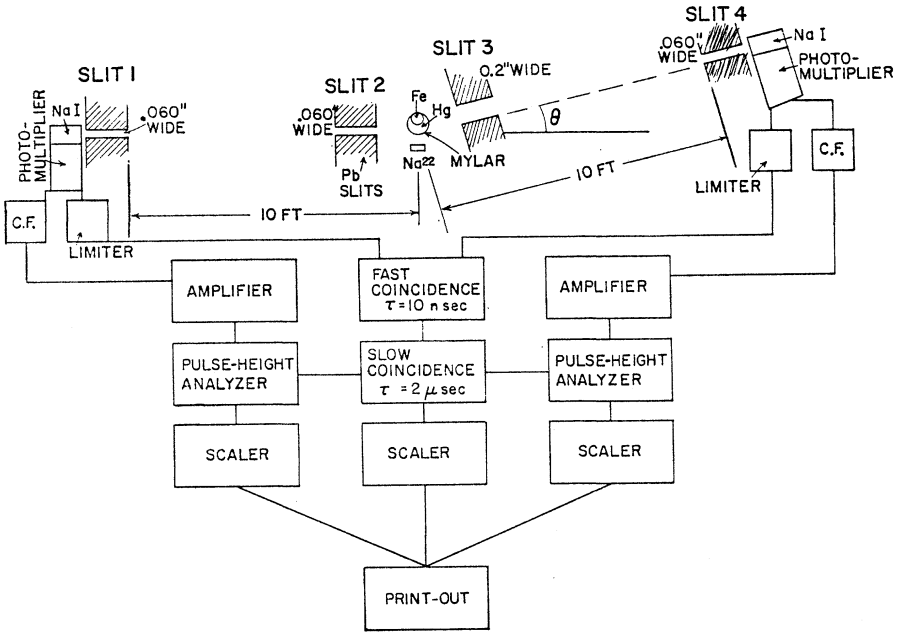

FIG. 1. Schematic diagram of the apparatus.

clusions about the electronic structure of both the solid and the liquid.

EXPERIMENTAL PROCEDURE

The angular correlation of the annihilation photons from the mercury was measured with a parallel slit system, shown schematically in Fig. 1. This geometry has been used and discussed by several other investigators.[7,8] Slits 1 and 2, the mercury sample, and the Na^{22} positron source were stationary while slits 3 and 4 were mounted on a movable arm which was pivoted about an axis through the sample. Slits 1 and 4 shielded the detectors while slit 2 defined the region of the mercury sample from which photons could be received and also shielded the stationary detector from the direct radiation of the Na^{22} source. These three slits were all 0.060 in. wide, thus defining an angular resolution of 0.5 mrad. Slit 2 was adjusted so that the Na^{22} source and the iron support rod were outside the region defined by it and slit 1. Only the mercury and its Mylar container were therefore visible to the stationary detector. Slit 3 served only to shield the movable detector from the Na^{22} source and was much wider than the other slits. Since the detectors only registered coincident photons, all measured annihilations took place in the region of the mercury and the Mylar, defined by slits 1 and 2.

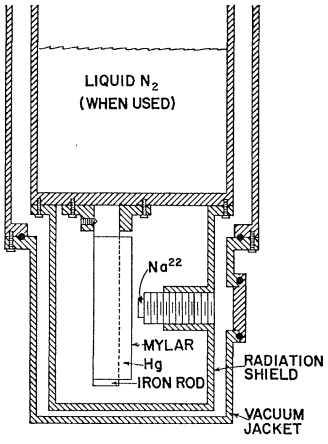

FIG. 2. The cryostat and sample holder.

A detail of the mercury sample and the Na^{22} positron source is shown in Fig. 2. 10 mC of Na^{22} were deposited in a depression in the end of the brass screw and covered with 0.25-mil Mylar. The distance between the source and the sample was adjusted by means of the screw to be about $\frac{1}{16}$ in. for this experiment. An iron rod was used to support the cylinder of 0.25-mil Mylar which was filled with triply distilled liquid mercury. Iron was chosen for the support because it is a fairly good conductor of heat and does not amalgamate with mercury. Slits were cut in the radiation shield and in the vacuum jacket to minimize scattering of the photons, those in the vacuum jacket being covered with 5-mil Mylar. The sample chamber was evacuated to minimize annihilation in the air and to provide thermal insulation for the low-temperature run. For the measurements on the solid, liquid nitrogen was added to the cryostat to freeze the mercury. No other changes were made in the apparatus between the two runs and the same Mylar covered the liquid and solid mercury.

Each detector consisted of two NaI(Tl) scintillation

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[8] S. Berko and J. S. Plaskett, Phys. Rev. **112**, 1877 (1958).

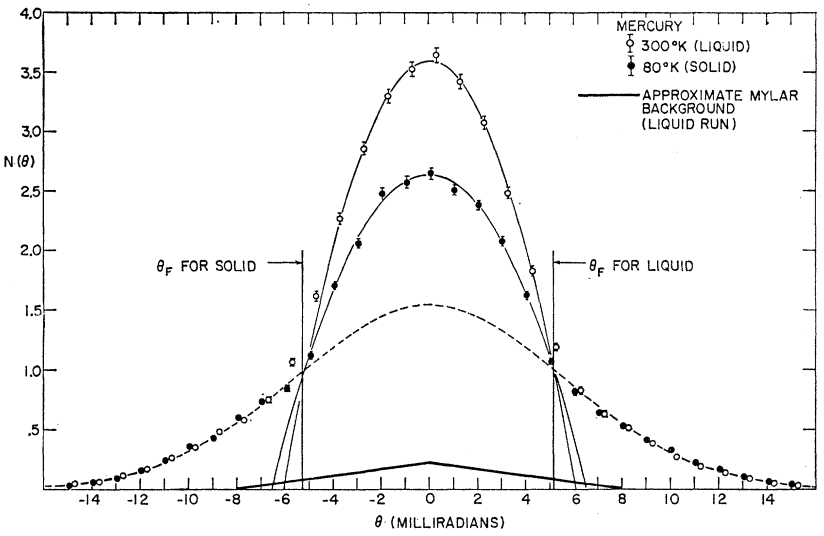

FIG. 3. The angular distribution of photon coincidences from liquid and solid mercury.

crystals in the form of disks of $\frac{1}{2}$-in. thickness and $1\frac{1}{2}$-in. diam. The crystals were arranged so that, including the slits, they made up a photon detector 3 in. long and 0.060 in. wide. Each of the four crystals was coupled to an RCA 6810 A photomultiplier tube; the gains of each pair were matched and the outputs added together. The photomultipliers were followed with a conventional fast-slow coincidence system[9] with an over-all resolving time of 10 nsec. The pulse-height analyzer following the movable detector was set to accept all pulses in the annihilation peak, while the other pulse-height analyzer was set to accept all pulses corresponding to an energy greater than 0.2 MeV.

The movable arm was programmed to sweep an arc extending 15 mrad each side of the central position, in steps of 1 mrad. The system was set to count for a fixed time at each position and was cycled over its 30 mrad angular range about 50 times in both the solid and liquid runs, in order to reduce the effects of drift in the electronics.

THE RESULTS

The angular distributions of annihilation coincidences for solid and liquid mercury are shown in Fig. 3. The zero of the abscissa is taken at the maxima of the least-squares parabolas which are fitted to the nine central points of each of the angular distributions. The centroids of the two angular distributions coincide with the maxima of the two parabolas.

It is possible, in principle, to calculate the angular distribution due to annihilation with core electrons from the core wave functions,[8] but since the principal interest in this experiment lay in the distribution from the conduction electrons, the core annihilation distributions were approximated by Gaussian functions. A Gaussian curve was fitted to those points outside 6 mrad for both the liquid and solid distributions, and the ordinate in Fig. 3 is normalized so that the areas under the two Gaussians are equal. Only the Gaussian for the liquid distribution is shown as the two curves were the same, within experimental error. As can be seen from Fig. 3, a Gaussian is a good approximation to the core annihilation distributions.

It is clear from Fig. 3 that the ratio of conduction electron to core annihilation changes significantly when the mercury solidifies. If we take the area under the Gaussian as being proportional to the number of core annihilations and that between the parabola and the Gaussian as proportional to the number of conduction electron annihilations, we find the percentages of core and conduction electron annihilations to be: liquid mercury—40% conduction, 60% core; solid mercury—25% conduction, 75% core.

In both the liquid and the solid results the Gaussian intersects the parabola at the angle, θ_F, corresponding to the Fermi wave vector for the free-electron model. In Fig. 4 the number of conduction electron coincidences, normalized to the maximum of the appropriate parabola, is plotted against θ/θ_F for both the solid and the liquid. It is noteworthy that, whereas the points for the solid do not deviate significantly from the parabola, there is a significant deviation near θ_F for the liquid.

The approximate background due to the Mylar container in the liquid run is shown in Fig. 3. It was not possible to determine the number of annihilations taking place in the Mylar accurately, because the shape of the container was different when the mercury was removed. Rough background measurements indicated, however, that about 7% of the annihilations occurred in the Mylar. Since the same Mylar covered the specimen in both the liquid and solid experiments, the differences between the two distributions could not have been caused by the container.

[9] *Beta- and Gamma-ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1955), pp. 502–505.

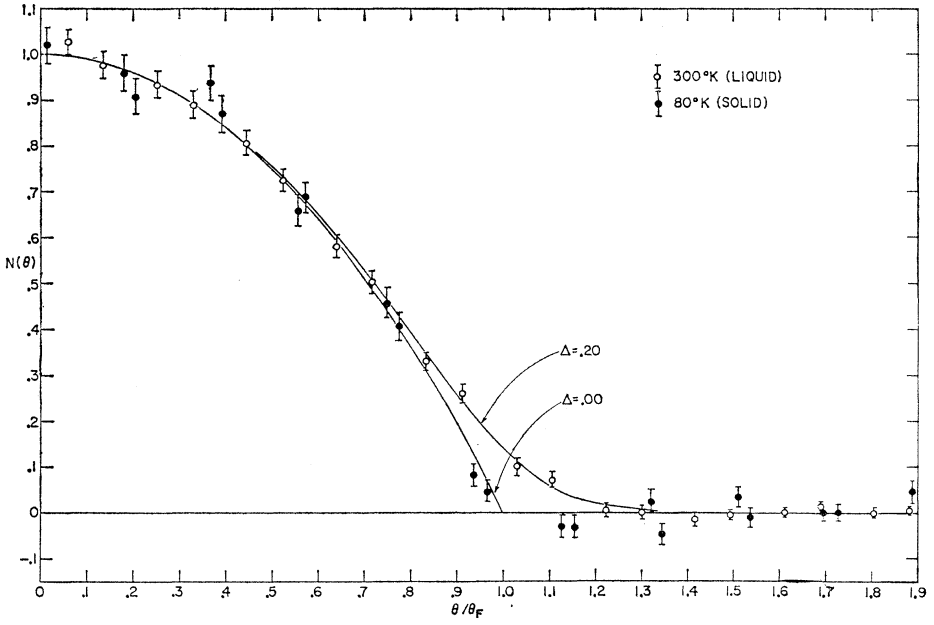

FIG. 4. The angular distribution of coincident photons from the conduction electrons in liquid and solid mercury, normalized to the maximum value. The solid curves are plots of Eq. (3).

DISCUSSION

The coincidences from the conduction electrons in the solid can be fitted, within the experimental error, to the parabola corresponding to a free-electron sphere containing two electrons per atom (see Fig. 4). This indicates that the Fermi surface in extended k space is comparatively little distorted from a sphere although the form of the surface in the reduced zone scheme is probably rather complex, on account of the complicated crystal structure of mercury. A parabolic distribution is also observed for such metals as sodium and potassium[6] which are thought to have almost spherical Fermi surfaces, while there are considerable departures from the free-electron parabola in the anisotropic metals, beryllium[10] and gadolinium.[11] The isotropy of the electronic distribution in mercury is not surprising, since there is considerable evidence that its neighbors in the periodic table, thallium[12] and lead,[13,14] do not depart greatly from the nearly free electron model.

The conduction electron coincidences from the liquid, on the other hand, depart significantly from the free-electron parabola. We interpret this as being due to the broadening of the conduction electron energy levels due to scattering of the electrons from the disordered lattice, and the consequent blurring of the Fermi surface. Explicit calculations of this effect have been made by Edwards.[1] In order to obtain an estimate of the magnitude of the uncertainty in wave vector, we assume that the probability of occupancy of a state k is given by

$$P(K)=A\{\exp[(K^2-1)/\Delta]+1\}^{-1}, \quad (1)$$

where A is a normalization constant, $K=k/k_F$ (k_F is the Fermi wave vector), and Δ is a parameter which describes the broadening of the energy levels. This function also describes the blurring of the Fermi surface due to an increase of temperature above the absolute zero. For an isotropic distribution of electrons in k space, the angular variation of coincidences is given by[5]

$$N(\beta)=2\int_\beta^\infty KP(K)dK, \quad (2)$$

where $\beta=\theta/\theta_F$. Substituting $P(K)$ from (1) in (2) and putting $A=1$ for convenience, we find

$$N(\beta)=(1-\beta^2)+\Delta\ln\{\exp[(\beta^2-1)/\Delta]+1\}. \quad (3)$$

As shown in Fig. 4, the angular distribution of the conduction electron coincidences in the liquid can be fitted quite well to such a function if Δ is taken as 0.20. If we take the uncertainty in wave vector as the difference between the values for which $P(k)$ is $\frac{1}{6}$ and $\frac{5}{6}$, respectively, and take into account the instrumental resolution ($\frac{1}{2}$ mrad at $\theta_F=5.16$ mrad) we find that $\delta k/k_F$ is approximately $20\pm5\%$. This value is somewhat greater than the approximate value of 6% estimated by Knight, Berger, and Heine[15] from the conductivity of the liquid. From a study of the temperature dependence of the resistivity, however, Ziman[16] has concluded that the

[10] A. T. Stewart, J. B. Shand, J. J. Donaghy, and J. H. Kusmiss, Phys. Rev. **128**, 118 (1962).
[11] D. R. Gustafson, A. R. Mackintosh, and D. J. Zaffarano (to be published).
[12] J. A. Rayne, Phys. Letters **2**, 128 (1962).
[13] A. V. Gold, Phil. Trans. Roy. Soc. **A251**, 85 (1958).
[14] A. R. Mackintosh, Proc. Roy. Soc. London **A271**, 88 (1963).
[15] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) 8, 173 (1959).
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Fermi surface area in the solid is only about half the free-electron value. If the nearly free electron model for liquid mercury is valid therefore, the Fermi surface area is approximately doubled on melting, so that the mean free path must be correspondingly shorter to explain the conductivity. Our value of δk implies a mean free path of the order of the 7 Å deduced from the nearly free electron model by Bradley, Faber, Wilson, and Ziman.[4]

The other interesting feature of the results is the change in the ratio of annihilations with the core and conduction electrons, on melting. In the solid the atomic radius is 1.76 Å, while the Goldschmidt ionic radius is 1.10 Å, so that the ions occupy approximately 25% of the volume of the metal. Since they contribute 75% of the annihilations, the probability per unit volume of a positron's annihilating in the ionic cores is roughly nine times greater than that in the remainder of the metal. Since there are 78 electrons in the Hg^{++} ionic core and only two conduction electrons per atom, the probability of annihilation with a single core electron is much smaller than that with a conduction electron, which is a natural consequence of the repulsion between the positively charged nucleus and the positron. There is a volume increase of approximately 6% on melting so, assuming that the ionic radius remains the same, the ion cores occupy approximately 23% of the volume of the liquid. Since the ionic cores now account for 60% of the annihilations, the probability per unit volume of annihilation in the core is approximately five times that in the rest of the metal.

This change indicates that the wave functions in the metal must be modified on melting in such a way that the product of the positron and conduction electron wave functions, which determines the annihilation probability,[7] must be relatively increased in the liquid. The effective pseudopotential seen by the electrons is comparatively small, due to the extensive cancellation of potential and kinetic energies,[17] so we expect the conduction electron density to be fairly constant in both the solid and liquid. On the other hand, there is no such cancellation for the positron, which sees a large repulsive potential at the ionic cores. The disorder of the ions in the liquid should, therefore, cause a considerable distortion of the positron wave function. In particular, when two ions approach each other both the potential and kinetic energies of a positron situated between them tends to increase, and it will therefore tend to move away from them, thus reducing the annihilation probability with the core electrons. There is no strong countervailing tendency for the positrons to move towards the ions when they are widely separated, so the net effect of the disorder is to increase the relative probability of annihilation with the conduction electrons. It would be interesting to make positron lifetime measurements in liquid and solid mercury to explore this effect further.

We conclude, therefore, that the disorder in the liquid phase produces a considerable broadening of the electronic energy levels in a metal, apart from purely thermal effects, and also modifies the wave functions, particularly, probably, those of the positrons. It would clearly be valuable to study other liquid metals using the same technique, with better resolution and statistics, and using smaller angular intervals. Of particular interest are the metals gallium and bismuth, which can increase their conductivity on melting. We are currently carrying out a detailed study of liquid and solid gallium.

ACKNOWLEDGMENTS

We are grateful to Professor M. G. Stewart for valuable assistance in the construction of the apparatus, and to Dr. V. Heine for sending us copies of his work prior to publication.

[17] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).