

## Positron Annihilation in Condensed Gases

D. C. LIU AND W. K. ROBERTS

*Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio*

(Received 4 February 1963)

The time distributions of positron annihilation in condensed  $H_2$ , He,  $N_2$ , and  $O_2$  have been measured. The free positron annihilation lifetime,  $\tau_1$ , for each substance shows a gross density dependence within a single phase and across the liquid-solid phase transition. For these materials studied  $\tau_1$  is shorter than that predicted by the spin-averaged cross section for the  $1S$  state annihilation pair and varies directly with  $E_i/\rho_e$ —the ratio of the first electron ionization potential to the outer shell electron density. Positronium is formed in all these substances. The orthopositronium pickoff lifetime,  $\tau_2$ , appears to be sensitive to the liquid-solid phases change in  $H_2$  and  $N_2$  but insensitive to the normal-superfluid state transition in He.

### I. INTRODUCTION

UNTIL recently, the free positron annihilation lifetime,  $\tau_1$ , in liquids and solids was thought to be constant despite large variations in electron density from one material to another. With the advent of the nanosecond vernier time-delay analyzer and time-to-pulse-height converter, Bisi *et al.*<sup>1</sup> and Bell and Jørgensen<sup>2</sup> were able to measure the difference in  $\tau_1$  among metals and to interpret the annihilation rate in terms of the radius of the unit electron sphere of the metal. Daniel and Stump<sup>3</sup> have shown that  $\tau_1$  in gaseous He is inversely proportional to the gas density but independent of the temperature. However, for condensed molecular substances, no experimental demonstration or theoretical treatment of the dependence of  $\tau_1$  on density, temperature or other molecular parameters has been reported. In the present research, we studied the time distributions of positron annihilation in various condensed gases as a function of density within a solid or liquid single phase, and across their melting points. Condensed gases were chosen because it is comparatively easy to vary the density, and their relatively simple molecular structures may facilitate the physical interpretation of the annihilation process.

Experimental verification of the existence of positronium in gases was first reported by Deutsch,<sup>4</sup> following an earlier observation by Shearer and Deutsch,<sup>5</sup> that the positron lifetime in certain gases at low pressures is not inversely proportional to the pressure. In many molecular substances, aside from the  $\tau_1$ , there may be present also a longer mean life,  $\tau_2$ , which is attributed to the para annihilation of a positron bound in orthopositronium with a lattice electron—a process which is generally referred to as the pickoff annihilation. This  $\tau_2$  component has been reported to be sensitive to temperature, density, and physical state of the annihilating medium.<sup>6</sup> Recently, we have reported<sup>7</sup> a very long  $\tau_2$  in

condensed  $H_2$ . It was also found that  $\tau_2$  doubles following a phase change at melting while  $\tau_2$  in the gaseous state at comparable densities differs little from that of the solid  $H_2$ . This implies that the  $\tau_2$  in  $H_2$  is phase sensitive. The present work extended the investigation of  $\tau_2$  in He,  $N_2$ , and  $O_2$ .

### II. EXPERIMENTAL METHOD

The experimental setup used in this work has been described in a preceding report.<sup>7</sup> Some necessary alterations were made on the time delay coincidence circuit in order to measure the faster  $\tau_1$ . The two gamma-ray detectors, placed at right angles with each other, consisted of NE102 plastic scintillators optically coupled to 56AVP photomultipliers. The pulse from the anode of the 56AVP was limited and sent on to a transistorized time-to-pulse-height converter similar to that described by Simms.<sup>8</sup> The remainder of the circuitry was essentially that used previously. The system was calibrated by inserting various lengths of RG71/U coaxial cable delaying the output pulse from one of the counters and observing the amount of centroid shift of the time distributions. The full width at half-maximum height for a  $Co^{60}$  curve is 1.0 nsec.

The time distribution of positron annihilation in a sample was measured by analyzing the distribution of the delayed coincidence between the 1.27 MeV nuclear gamma ray accompanying the creation of each positron and the 0.51 MeV gamma ray resulting from destruction. The mean life was deduced by drawing a best-fit straight line through the data points of the logarithmic count rate vs time delay plot. By this method, the positron mean life in aluminum is  $0.20 \pm 0.02$  nsec, which is in good agreement with the latest value reported by Bell and Jørgensen.

The  $H_2$ , He,  $N_2$ , and  $O_2$  used were commercial cryogenic liquids, used as received. Temperature or density variations of the liquid and solid phases were

<sup>1</sup> A. Bisi, G. Faini, E. Gatti, and L. Zappa, *Phys. Rev. Letters* **5**, 59 (1960).

<sup>2</sup> R. E. Bell and M. H. Jørgensen, *Can. J. Phys.* **38**, 652 (1960).

<sup>3</sup> T. B. Daniel and R. Stump, *Phys. Rev.* **115**, 1599 (1959).

<sup>4</sup> M. Deutsch, *Phys. Rev.* **82**, 455 (1951); **83**, 866 (1951).

<sup>5</sup> J. W. Shearer and M. Deutsch, *Phys. Rev.* **76**, 462 (1949).

<sup>6</sup> See review articles: (a) S. Berko and F. L. Hereford, *Rev. Mod. Phys.* **28**, 299 (1956); (b) S. DeBenedetti and H. C. Corben, *Ann. Rev. Nucl. Sci.* **4**, 191 (1954); (c) R. A. Ferrell, *Rev. Mod.*

*Phys.* **28**, 308 (1956); (d) P. R. Wallace, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 1.

<sup>7</sup> D. C. Liu and W. K. Roberts, *J. Phys. Chem. Solids* **23**, 1337 (1962).

<sup>8</sup> P. C. Simms, *Rev. Sci. Instr.* **32**, 894 (1961).

TABLE I. Mean lives of positrons in condensed gases.

Substance	$E_i^a$ (V)	$\rho_e^b$ ( $10^{-3} a_0^{-3}$ )	$\tau_1$ (nsec)		$\tau_2$ (nsec)	
			Liquid <sup>c</sup>	Solid <sup>d</sup>	Liquid <sup>e</sup>	Solid <sup>d</sup>
Oxygen	12.5	25.5	0.45 ± 0.02	...	...	...
Nitrogen	15.5	15.5	0.56 ± 0.02	0.48 ± 0.02	10.8 ± 0.9	4.9 ± 0.4
Hydrogen	15.6	6.32	0.92 ± 0.04	0.80 ± 0.03	28.6 ± 2.3	14.6 ± 1.2
Helium	24.5	5.57	1.90 ± 0.06	...	88.0 ± 7.5	...

<sup>a</sup> Values are taken from the *Handbook of Chemistry and Physics*, edited by Charles D. Hodgman (The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962), 44th ed.

<sup>b</sup> Values are calculated from  $\rho_e = L\rho Z/A$  in units of  $10^{-3} a_0^{-3}$ , where  $L$  is Avogadro's number,  $\rho$  is the gross density in g/cm<sup>3</sup>,  $Z$  is the number of outer shell electron,  $A$  is the atomic weight, and  $a_0$  is the first Bohr radius in cm.

<sup>c</sup> Liquids are at normal temperature of ebullition.

<sup>d</sup> Solids are at 1° below normal melting point.

<sup>e</sup> No  $\tau_2$  component was observed.

achieved by pumping, controlled by a cartesian manostat.

### III. RESULTS

The great similarity of the time distribution curves among all of the condensed gases makes it of little value to display all of the original data curves. Instead, the mean lives at the normal boiling points and near the melting points are summarized in Table I. Each value shown in Table I is the average of several runs. The assigned error for the mean lives represents the extremes of the range of deviations of individual measurements from the average value shown. No mean-life measurement on solid He and O<sub>2</sub> was made since the solid phase in these two materials cannot be conveniently achieved by pumping. The variation of the free positron annihilation rate,  $\lambda_1 = 1/\tau$ , with gross density,  $\rho$ , is depicted in Fig. 2.

### IV. DISCUSSION

#### A. Free Positron Annihilation

On examination of Table I one sees that, in general,  $\tau_1$  increases with decreasing  $\rho_e$ , the outer shell electron density, and that  $\tau_1$  increases with increasing  $E_i$ , the first electron ionization potential. The observed  $\tau_1$  for each substance is shorter than that predicted by the Dirac annihilation cross section for the 1S state annihilation pair, neglecting Coulomb attraction.

The inverse relationship between  $\tau_1$  and  $\rho_e$  is generally established experimentally and theoretically in metals. Our present  $\tau_1$  values show only the general correct order in variation with  $\rho_e$ . A quantitative agreement is not observed. We see here a large difference in  $\rho_e$  between O<sub>2</sub> and N<sub>2</sub> gives only a small difference in  $\tau_1$  while a small difference in  $\rho_e$  between H<sub>2</sub> and He gives a large difference in  $\tau_1$ . From these results it appears that  $\tau_1$  is sensitive to other parameters besides  $\rho_e$ .

The same ordering of the observed  $\tau_1$  and  $E_i$  is reasonable since, in the annihilation process in a molecular substance where electron exchange takes place only within the individual molecule, the positron must pull an electron away from the molecule. The material whose electrons are tightly bound in a molecule would,

thus, show a longer annihilation lifetime, and conversely for a material whose electrons are loosely bound. However, no perfectly quantitative agreement is expected in a simple dependence of  $\tau_1$  on  $E_i$  alone. We see here that  $\tau_1$  for N<sub>2</sub> differs considerably from the  $\tau_1$  for H<sub>2</sub> although the  $E_i$ 's for these two molecules are nearly the same. The reason may lie in the difference in their  $\rho_e$ 's.

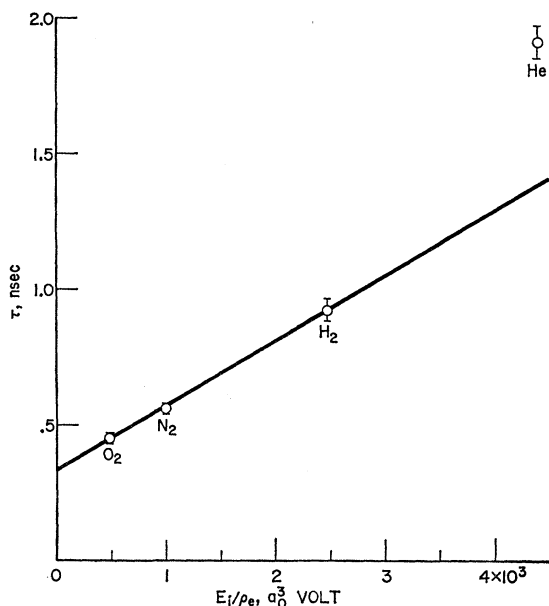
From the foregoing discussion, it would appear that  $\tau_1$  may be dependent on the combined effect of  $E_i$  and  $\rho_e$ . Figure 1 shows a plot of  $E_i/\rho_e$  vs  $\tau_1$  for the liquids at their normal boiling point. A good fit is observed except that the value for He is large by about 30%. This discrepancy is not surprising because we are using for  $\rho_e$  the average electron density instead of the actual electron density at the position of the positron. Let us compare the situation in a He atom with that in a H<sub>2</sub> molecule. In their ground states, both have the complete shell characteristics and have nearly the same average electron density. However, the probability distributions of the charge of the two electrons in these substances are different. This distribution is spherical around the He nucleus but is relatively confined to a region between the two nuclei in the H<sub>2</sub> molecule. For this reason, a positron would experience relatively more repulsion in approaching a He atom than in approaching a H<sub>2</sub> molecule, thus resulting in a lower annihilation rate or a longer mean life in the He.

We see also in Fig. 1 that an extrapolation to  $E_i/\rho_e = 0$  gives an intercept at  $\tau_1 = 0.33$  nsec which may be thought of as the positron mean life in a plasma in which there are no bound electrons, so that no work is required of the positron to capture an electron. This value agrees well with the average positron lifetime (0.36 nsec) in the alkali metals for which the "free electron gas" model is most valid.

Each part of Fig. 2 shows a plot of both the free positron annihilation rate,  $\lambda_1$ , and gross density,  $\rho$ , as a function of temperature for a particular condensed gas. For each material, the range of  $\lambda_1$  measured is about three times the assigned error.

The He data are depicted in Fig. 2(a). We see that  $\lambda_1$  increases with  $\rho$  down to the lambda point region, while both  $\lambda_1$  and  $\rho$  are nearly constant at temperature below the lambda point. At 1.5°K liquid He is essentially in the superfluid state, yet  $\lambda_1$  at that temperature is nearly the same as that of the normal liquid He at few tenths of a degree above the lambda point. These results demonstrate that  $\lambda_1$  in He is sensitive to density change but insensitive to the normal-superfluid state transition.

Parts (b) and (c) of Fig. 2 depict the H<sub>2</sub> and N<sub>2</sub> data, respectively. In both substances,  $\lambda_1$  varies directly with  $\rho$  within a single phase as well as across the melting point transition. This demonstrates that  $\lambda_1$  is density-dependent and is also insensitive to the liquid-solid phase change. Of interest here is also the  $\rho$ - $T$  curve drawn as a best fit through the solid N<sub>2</sub> data points,

FIG. 1.  $\tau_1$  dependence on  $E_i/\rho_e$ .

since no direct measurement of the density of solid  $N_2$  has been reported in the literature. The density of solid  $N_2$  thus deduced from the positron measurement is  $0.980 \pm 0.035$  g/cm<sup>3</sup> in the vicinity of its melting point.

A direct variation of  $\lambda_1$  with  $\rho$  in liquid  $O_2$  was also observed but with less certainty. Since the maximum change possible in  $\rho$  within the liquid phase under its own vapor pressure is about 10%, only the change between the  $\lambda_1$ 's at the extreme limits of  $\rho$  is outside of the experimental error of  $\pm 4.5\%$ . It was found that  $\lambda_1 = (2.23 \pm 0.10) \times 10^9$  and  $(2.45 \pm 0.11) \times 10^9$  sec<sup>-1</sup> at  $\rho = 1.15$  and  $1.28$  g/cm<sup>3</sup>, respectively. Between smaller differences in  $\rho$  the change in  $\lambda_1$  is qualitative but generally in the correct direction.

### B. Orthopositronium Pickoff Annihilation

The orthopositronium pickoff annihilation is the singlet annihilation of a lattice electron with a positron bound in orthopositronium. The lifetime of this process is generally designated as  $\tau_2$ . We observed a  $\tau_2$  component in condensed  $H_2$ , He, and  $N_2$  but not in liquid  $O_2$ . However, positronium is also formed in  $O_2$ . This is evident from the presence of a weak 0.2 nsec component arising from the parapositronium in the time distribution curve of liquid  $O_2$ . This is also observed in the other three condensed gases studied. The absence of the  $\tau_2$  in liquid  $O_2$  is due to the quenching of the orthopositronium by the paramagnetic  $O_2$  molecule. In this process the orthopositronium is converted to parapositronium by exchanging spin with an electron in the  $O_2$  which has two electron spins parallel.

We have reported elsewhere<sup>7</sup> that  $\tau_2$  in  $H_2$  is sensitive to phase changes. A similar result is observed here in

condensed  $N_2$ .  $\tau_2$  is  $10.8 \pm 0.9$  nsec for liquid  $N_2$  at the normal boiling point (77.3°K at 1 atm) and is  $4.9 \pm 0.4$  nsec for the solid at 62.0°K ( $\sim 1^\circ$  below the normal melting point). Within the limit of the experimental error,  $\tau_2$  is unchanged by a small density change within a single (liquid or solid) phase. The doubling of  $\tau_2$  as the melting point is passed thus suggests that the effect involved is more than can be accounted for by the small change in gross density alone.

The presence of an extremely long  $\tau_2$  in liquid He was first observed by Paul and Graham<sup>9</sup> and Wackerle and Stump<sup>10</sup> and was the subject of much discussion<sup>6d,11</sup> and further experiments.<sup>3</sup> Our interest consists simply

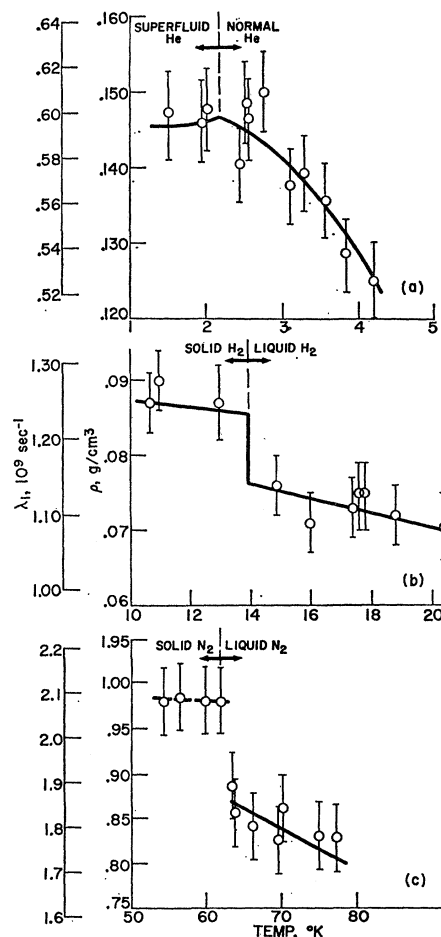


FIG. 2. Plots of both  $\lambda_1$  and  $\rho$  as a function of  $T$  for (a) He, (b)  $H_2$ , and (c)  $N_2$ . The points are the  $\lambda_1$  values. The  $\rho$ - $T$  curve for He is drawn with data taken from Table II in *Liquid Helium* by K. R. Atkins. The  $\rho$ - $T$  curves for  $H_2$  and liquid  $N_2$  are drawn with extrapolation from data taken from *Cryogenic Data Book*, UCRL-3421. The dashed curve in (c) is a best fit through the  $\lambda_1$  data points, giving the  $\rho$  for solid  $N_2$  in the  $T$  range.

<sup>9</sup> D. A. L. Paul and R. L. Graham, *Phys. Rev.* **106**, 16 (1957).

<sup>10</sup> J. Wackerle and R. Stump, *Phys. Rev.* **106**, 18 (1957).

<sup>11</sup> R. A. Ferrell, *Phys. Rev.* **108**, 167 (1957).

in an attempt to correlate  $\tau_2$  with the gross density within the liquid phase and through the normal-superfluid transition. Again, within the limit of experimental error we detected no difference in  $\tau_2$  by an

approximately 15% change in liquid density as well as between the normal and superfluid states at comparable density. The latter result confirms Paul and Graham's observation.

PHYSICAL REVIEW

VOLUME 130, NUMBER 6

15 JUNE 1963

## Low-Lying Energy Levels of Lanthanide Atoms and Intermediate Coupling\*

J. G. CONWAY AND B. G. WYBOURNE†

*Lawrence Radiation Laboratory, University of California, Berkeley, California*

(Received 5 February 1963)

A detailed examination of the effects of intermediate coupling on the properties of the low-lying levels of lanthanide atoms has been made. Particular attention has been given to the effects of a breakdown of Russell-Saunders coupling on the energies and magnetic properties of the levels of the ground multiplets. The energy levels were calculated by diagonalization of the combined electrostatic and spin-orbit matrices of the  $f^n$  configurations. It is found possible to fit the energy levels of the ground multiplets of Nd I and Sm I to within  $2 \text{ cm}^{-1}$  of their observed energies using  $4f$ -hydrogenic ratios for the Slater  $F_k$  integrals. The  $g$  values are found to agree within the experimental errors of the atomic beam measurements. An explanation for the apparent success of the  $4f$ -hydrogenic eigenfunctions is offered and it is demonstrated that the success of these eigenfunctions does not imply that the actual eigenfunctions are hydrogen-like. Tables of the calculated energies and eigenvectors for low-lying levels are given together with the  $g$  values calculated in intermediate coupling. The effects of intermediate coupling on the relativistic and diamagnetic corrections to the  $g$  values are examined and shown to fall within the range of atomic beam measurements. The importance of intermediate coupling in the actinides is noted.

### INTRODUCTION

IN recent years the application of the techniques of atomic beam resonances has led to very precise measurements of the  $g$  values associated with the levels of the ground multiplets of the atoms belonging to the first rare earth series, the lanthanides. Measurements of the hyperfine structure of the levels of these multiplets has permitted the evaluation of the nuclear magnetic and electric quadrupole moments of the atoms. Spectroscopic studies have succeeded in establishing all the energy levels of the ground multiplets of the Nd I and Sm I atoms. Except for Ce I, Gd I, and Tb I, the ground multiplets have been established as belonging to the  $4f^n 6s^2$  configurations.

In a recent paper, Judd and Lindgren<sup>1</sup> have examined the Zeeman effect for the ground multiplets in considerable detail. They have made several corrections to the simple Lande' formula for the  $g$  values of the levels deriving from the ground terms of configurations of the type  $4f^n$ . Among these, they attempted to (a) correct for deviations from perfect Russell-Saunders coupling, (b) correct for relativistic and diamagnetic effects. To calculate the spin-orbit corrections it was necessary to estimate the Slater integrals  $F_k$  and the spin-orbit coupling constants  $\zeta_{4f}$ . The ratios of the integrals  $F_k$

were assumed to be those calculated for a  $4f$ -hydrogenic eigenfunction.

In the present paper it is shown that the energy levels of the ground multiplets of the lanthanide atoms are very sensitive to the magnitude of the spin-orbit coupling constants and relatively insensitive to the precise form of the Coulomb interaction. It is found that the remarkably close agreement between the calculated and experimental  $g$  values obtained by Judd and Lindgren<sup>1</sup> does not imply that the  $4f$  eigenfunctions for the lanthanides are necessarily even to a close approximation, hydrogen-like. Calculations of the spin-orbit corrections to the  $g$  values were made by diagonalizing the energy matrices of the appropriate  $4f^n$  configurations. The eigenvectors obtained from these diagonalizations are tabulated and used to obtain accurate intermediate coupling corrections for the  $g$  values. An attempt has been made to obtain reliable estimates of the energies of the levels of the ground multiplets which in many cases still have to be established experimentally.

### ENERGY LEVELS OF Nd I AND Sm I

Schuermans<sup>2</sup> has established all the levels of the  $4f^4(^5I)6s^2$  multiplet of Nd I while Albertson<sup>3</sup> has established those of the  $4f^6(^7F)6s^2$  multiplet of Sm I. The complete energy matrices for the  $f^4$  configuration have

\* Work done under the auspices of the U. S. Atomic Energy Commission.

† Present address: Division of Chemistry, Argonne National Laboratory, Lemont, Illinois.

<sup>1</sup> B. R. Judd and I. Lindgren, *Phys. Rev.* **122**, 1802 (1961).

<sup>2</sup> Ph. Schuermans, *Physica* **11**, 419 (1946).

<sup>3</sup> W. Albertson, *Phys. Rev.* **52**, 644 (1937).