

FIG. 1. Representative set of delay curves at various temperatures. The 29°C curve shows the analysis of the component lifetime curves. The melting point is at 80.2 degrees.

80.2°C. No attempt has been made to form single crystals, polycrystalline naphthalene being used. The annihilation lifetimes were measured with a Bell and Graham type fast-coincidence circuit, Na²² being the positron source. The percentage of positrons annihilating in the source holder was estimated to be less than 6%. This estimate was obtained by analysis of curves taken below the melting point with Na²² deposited directly on naphthalene. Three different samples were run, samples II and III with improved temperature regulation (better than $\pm 0.1^\circ\text{C}$); lifetime delay curves were taken at varying temperatures. Figure 1 shows a set of four representative delay curves, the first of these (29°C) being plotted with its analysis into the two lifetime curves (obtained by the usual folding technique). Figure 2 shows the curve of τ_2 vs temperature. The points are plotted with errors computed from the least squares fitting of τ_2 for the individual runs; the larger point-to-point deviations are due to electronics and possibly differences in crystallinity of the naphthalene from sample to sample.

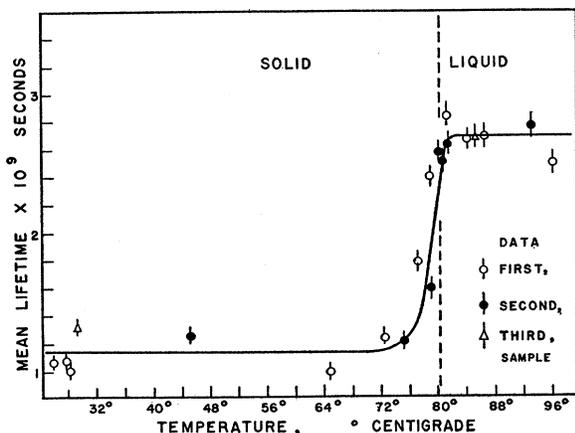


FIG. 2. The curve of τ_2 vs temperature. The full line is a visual fit to the experimental points. The melting point is 80.2°C.

From these curves we see that below the melting point about 9% of positrons annihilate via a τ_2 component, $\tau_2 = 1.14 \times 10^{-9}$ sec, with τ_2 starting to rise a few degrees below melting and reaching the value of $\tau_2 = 2.68 \times 10^{-9}$ sec at and above the melting point. The percentage of positrons annihilating with τ_2 increases sharply from 9% to 29%, the change occurring within 0.2°C of the melting point. The short lifetime, τ_1 , was of the order of $(3-4) \times 10^{-10}$ sec for all curves analyzed.

From these measurements we draw the following conclusions:

(a) The capture cross section of positrons into bound states has a sharp increase above melting. Besides the energetics of the capture process (similar to "Ore gap"³ in gases), there could exist other selection rules (conservation of momentum) that are relaxed upon destruction of long-range order during melting.

(b) Whatever the processes giving rise to triplet decay via τ_2 , the cross sections of these processes are enhanced in the ordered crystalline state. Since the change in τ_2 is less sudden than that in the percentage annihilating with τ_2 , perhaps short-range effects are here more important. The possibility of Van der Waals binding of positronium to the molecules of the crystal⁴ could play a role.

We have also observed similar order-disorder effects in Teflon of differing crystallinities; a complete report on this work will follow shortly.

We thank Dr. John S. Plaskett of our laboratory for discussions relating to the theoretical aspects of this problem.

* Alfred P. Sloan Research Fellow, 1955-1956.

† National Science Foundation Predoctoral Fellow, 1955-1956.

¹ R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).

² Berko, Stephan, Zuchelli, and Joseph, Phys. Rev. **102**, 724 (1956); V. L. Telegdi, Bull. Am. Phys. Soc. Ser. II, **1**, 168 (1956).

³ A. Ore, University of Bergen Yearbook, Nos. 9, 12 (Bergen, Norway, 1949).

⁴ P. R. Wallace, Phys. Rev. **100**, 738 (1955).

Ground State Energy of Two-Electron Atoms

EGIL A. HYLLEAAS AND JOHN MIDTAL

Institute for Theoretical Physics, University of Oslo, Oslo, Norway

(Received June 6, 1956)

THE nonrelativistic energies for the ground states of ions and atoms: H^- , He, Li^+ , \dots , have been recalculated by means of an electronic computer using 18 and finally 24 terms in the wave functions. Besides terms of the familiar type: $e^{-s/2}$ times 1, s , u , s^2 , l^2 , u^2 , su , \dots , up to the fifth and sixth degrees, 4 additional terms:

$$P_1 = \left[\frac{1}{2}(s^2 + l^2) - u^2 \right] \log s, \quad P_2 = \left[\frac{1}{2}(s^2 + l^2) - u^2 \right] u/s, \\ s l^2/u, \quad \text{and} \quad s l^4/u^3,$$

TABLE I. $-E_2(\infty)/Rh$.

s	0.195 312 5	P_1	0.000 120 9
u	96 955 1	P_2	194 6
f^2	14 737 4	s^2/u	65 7
s^2	0 0	st^4/u^3	34 7
u^2	5 780 4		
su	419 1	u^2f^2	6 9
u^2	803 9	u^4	0 9
u^3	625 5	s^2u^2	0 0
st^2	8 9	s^4	3 8
s^2u	236 4	t^4	3 0
s^3	1 6	u^5	0 0
		Sum:	0.315 311 3

originating from a nonconvergent logarithmic expression appearing in the formal solution of the wave equation, have been used. The new terms are very effective at an early stage of the calculations. It is doubtful, however, whether they lead to another limiting value of the energy. At the end of the calculations the improvement in energy values for which the four new terms are responsible, shrinks down to the order of $2-5 \text{ cm}^{-1}$ in spectroscopic units.

In the following we shall use the notation $E = -2Z^2 + (5/4)Z + E_2$ for the total energy in Rh -units. In the case of $Z \rightarrow \infty$, the E_2 value has been brought down considerably, first from $-E_2 = 0.30488$ to 0.30526 by ordinary terms, and finally in a very high approximation, comprising the above-mentioned new terms, to 0.30531 . At the other end, at $Z=1$, the calculated energy of H^- has also been considerably improved, so that the value $-E_2 = 0.30512$ as given in the excellent work of Henrich,¹ can now be replaced by $-E_2 = 0.30545$. For Li^+ , Be^{++} , \dots , O^{6+} , \dots , there are improvements on a somewhat smaller scale. For He the accuracy has already been very effectively extended by Chandrasekhar and Herzberg.² Nevertheless we have succeeded in improving even the value of the He ground state energy by about 2 cm^{-1} .

In Table I we demonstrate the contributions from various terms to the ground state energy for $Z \rightarrow \infty$, giving thereby also some information about the terms involved in the (here 22-parameter) wave function.

Table II gives some historical data concerning the improvements in the H^- energy. Finally in Table III

TABLE II. Energy values for H^- .

	Appr.	$-E_2/Rh$
Bethe and Hylleraas 1930	3	0.3006
Williamson 1942	6	0.30292
Chandrasekhar ^a	7	0.303808
Henrich ^b 1943	11	0.30512
Hylleraas 1954	12	0.305141
Present calc	18 ^c	0.305355
Present calc	18 ^d	0.305378
Present calc	24 ^d	0.305451

^a S. Chandrasekhar, *Revs. Modern Phys.* **16**, 301 (1944).

^b See reference 1.

^c Without the logarithmic terms.

^d Including the logarithmic terms.

TABLE III. Energies of various ions.

A	$-E_2(A)$	A	$-E_2(A)$
H^-	0.305451	F^{7+}	0.313426
He	0.307457	Ne^{8+}	0.313613
Li^+	0.309818	Na^{9+}	0.313766
Be^{2+}	0.311131	Mg^{10+}	0.313894
B^{3+}	0.311945	Al^{11+}	0.314003
C^{4+}	0.312496	Ca^{18+}	0.314459
N^{5+}	0.312893	\dots	\dots
O^{6+}	0.313192	$Z = \infty$	0.315311

we give the energy values of a series of ions corresponding to the formula:

$$E_2 = -0.315311 + \frac{0.01707}{Z} - \frac{0.00068}{Z^2} + \frac{0.00164}{Z^3} - \frac{0.00489}{Z^4}$$

This formula is so constructed as to give the directly computed energy values for H^- , He, and Li^+ with a compromise between the computed values for Be^{++} and O^{6+} . The latter value is almost exactly reproduced. The Be^{++} value comes out $0.000006Rh$ or 0.7 cm^{-1} lower than that really obtained by direct calculation using a 24-parameter wave function.

Fuller details of the calculations will be given elsewhere.

¹ L. R. Henrich, *Astrophys. J.* **99**, 59 (1943).

² S. Chandrasekhar and G. Herzberg, *Phys. Rev.* **98**, 1050 (1955).

Dielectric Behavior of Lead Titanate at Low Temperature

JINZO KOBAYASHI, SHIGEHARU OKAMOTO, AND RYUZO UEDA

Department of Applied Physics, Waseda University, Tokyo, Japan

(Received April 13, 1956)

LEAD titanate, PbTiO_3 , is known to be a BaTiO_3 -type ferroelectric with polar tetragonal symmetry from room temperature up to the Curie point, 490°C . Further x-ray investigation on the material, however, has revealed a low-temperature transition at about -100°C as reported previously. The new phase of PbTiO_3 is a superstructure in which the oxygen ions in different sublattices are considerably displaced in antiparallel directions. Thus the structural evidence leads to the possibility of an antiferroelectric state in PbTiO_3 at low temperature.

Heretofore, investigations of the dielectric properties of PbTiO_3 have not shown an anomaly corresponding to the onset of the superstructure at about -100°C . This may possibly be due to the measurements being performed on crystals which were cooled too quickly. To resolve the ambiguity, a critical re-examination of the low-temperature region seemed to be necessary. This paper describes our results on the dielectric properties of well purified PbTiO_3 at low temperature.

As the x-ray observations showed a markedly large