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
t^2	14 737 4	st^2/u	65 7
s^2	0 0	st^4/u^3	34 7
u^2	5 780 4		
su	419 1	u^2t^2	6 9
ut^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 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^{++}, $\cdots$, O^{6+}, $\cdots$, 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 we give the energy values of a series of ions corresponding to the formula:

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

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		$\cdots$
O^{6+}	0.313192		$Z=\infty$:0.315311

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.

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[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

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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

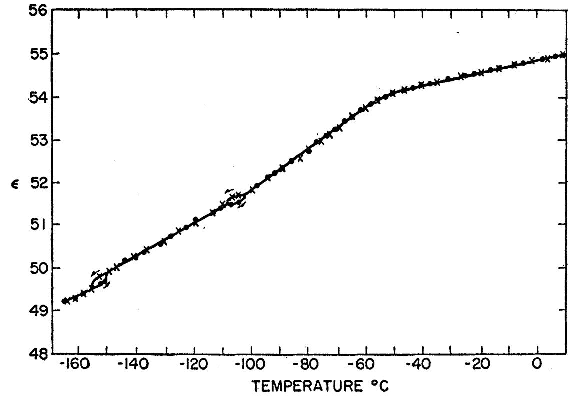

FIG. 1. Dielectric constant of $PbTiO_3$. The dots refer to rising temperature, the crosses to falling temperature.

thermal hysteresis in the transition, the present dielectric measurements with a weak field were carried out in such a way as to take this into account. The temperature dependence of ϵ is shown in Fig. 1. The cooling and heating rates were 0.3°C/min. The measments were performed by using a disk-shaped sample 0.96 cm in diameter and 0.13 cm thick, the frequency used being 1 Mc/sec. Two small but distinct anomalies in dielectric constant appear at about -100°C and -150°C. The anomaly at -100°C is rather small, but corresponds to the structural change discovered by x-rays. The anomaly at -150°C seems to suggest that a further transition takes place at this lower temperature. This transition, however, has not been confirmed by x-rays, for it is difficult to cool below -150°C in our x-ray camera. The trend of the temperature coefficient of variation of the dielectric constant changes gradually in the vicinity of -60°C.

Up to the present work it has been difficult to find support for antiferroelectricity in $PbTiO_3$ in the low-temperature region; but the minor changes in ϵ can be clearly observed both at -100°C and at -150°C and seem similar to those at 470°C and 520°C in $NaNbO_3$ found by Cross and Nicholson.

Considering the present result, it would seem necessary to make further studies on other ferroelectrics, especially on solid solutions with $PbTiO_3$, at low temperature.

[1] J. Kobayashi and R. Ueda, Phys. Rev. **99**, 1900 (1955).

[2] L. F. Cross and B. T. Nicholson, Phil. Mag. **46**, 453 (1955).

Vapor Pressure of the Solution of He³ in He⁴

S. K. TRIKHA AND V. S. NANDA
Department of Physics, University of Delhi, Delhi, India

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RECENTLY, Daunt and Tseng[1] have reported the difference in vapor pressure between a 4% solution of He^3 in liquid He^4 and pure liquid He^4 over a fairly wide range of temperatures. The experimental results are not in good agreement with the predictions of previous theories.[2–4]

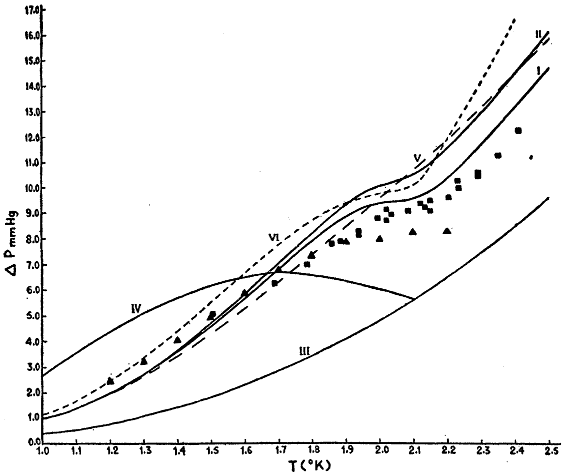

FIG. 1. The vapor pressure difference $\Delta P_{\mathrm{mm\,Hg}}$ $(=P-p_4{}^0)$ for a 4% solution of He^3 in He^4, as a function of absolute temperature T(°K). Curve I: present model, linear expression for G_4. Curve II: present model, quadratic expression for G_4. Curve III: perfect classical solution theory. Curve IV: de Boer and Gorter's theory.[2] Curve V: Heer and Daunt's theory.[3] Curve VI: Mikura's theory.[4] ▲: Smoothed experimental results of Sommers.[9] ■: Experimental results of Daunt and Tseng.[1]

According to a model recently proposed by us,[5,6] the expressions for the partial vapor pressures are

$$p_4=p_4{}^0(1-X_L)^x\exp\left\{\frac{1}{RT}[G_4(T,x)-G_4(T,x_0)+xX_L{}^2W-(P-p_4{}^0)B_{44}-PX_V{}^2\gamma]-X_L(1-x)\right\},$$

and

$$p_3=p_3{}^0X_L\exp\left\{\frac{1}{RT}[x(1-X_L)^2W-(P-p_3{}^0)B_{33}-P(1-X_V)^2\gamma]+(1-X_L)(1-x)\right\},$$

where X_L and X_V are the concentrations of He^3 in the liquid and the vapor phases respectively, $p_4{}^0$ and $p_3{}^0$ are the vapor pressures of He^4 and He^3 respectively in the pure phase; $P(=p_3+p_4)$ is the total pressure, $\gamma=2B_{34}-B_{33}-B_{44}$, the B's being the second virial coefficients; G_4 is the Gibbs' function for pure He^4; x is the fraction of the total number of atoms of He^4 which constitutes the normal fluid; $w=W/N$ is the interchange energy, and N is Avogadro's number.

Using the experimentally observed[7] value of $(\partial T_{\lambda X}/\partial X_L)_{X_L\to 0}$ and following the method outlined in reference 5, W is found to be 1.976 and 2.406 cal mole^{-1} for the linear and quadratic expressions of G_4, respectively.[8] The λ temperature of the solution, $T_{\lambda X}$, calculated by making use of both the expressions for G_4, is in excellent agreement with the experimental results.[7]