

excited in a dense vapor layer close to the liquid aluminum surface. The layer must be thin because if the gaseous Al atoms extended any appreciable distance from the anode, an arc or discharge would take place in the sample chamber. Such a discharge did not occur. If the source of the $K\beta$ band is in the gaseous layer above the sample, then we must assume that the continually narrowing band in the intermediate temperature range is due to a increase in concentration of Al atoms over the liquid. However, bands recorded in the intermediate range did not have the appearance of a composite of the narrow and broad bands. That is the intermediate bands retained the original asymmetrical shape but became narrower at the base. The penetration of 6-kV electrons even in a low- Z element like Al is not great. The range of low-energy electrons in solids has been studied by Feldman⁹ who shows that the range in angstrom units for electrons may be calculated by the equation

$$R(\text{\AA}) = 250A/\rho(E/\sqrt{Z})^n, \quad n = 1.2/(1 - 0.29 \log_{10} Z),$$

where A is the atomic weight, ρ is the bulk density in

⁹ C. Feldman, Phys. Rev. **117**, 455 (1960).

g/cc, E is the electron energy in keV, and Z is the atomic number. Substituting the appropriate values for aluminum we obtain a penetration depth in the solid of about 6000 \AA for 6-kV electrons. Therefore, if the electrons are to be completely absorbed in a layer of Al atoms on the surface, then this gaseous layer, if it exists, must appreciably exceed 6000 \AA since the density would be less than in the solid.

It has been suggested that perhaps an oxide layer or other contamination results in the effect shown here for $K\beta$. Such contamination does not account for the results shown here. We have shown previously that chemical combination of aluminum causes a gross shift to longer wavelengths in Al $K\beta$ and large changes in the $K\alpha_4/K\alpha_3$ ratio.⁶

Certainly, we have not proven in this paper that the observed narrow $K\beta$ originates from the liquid. Neither can we conclusively state that it originates in a vapor layer. We present our findings, however, with the hope that other workers using other techniques will investigate liquid aluminum at temperatures much higher than the melting point to determine if any real changes occur in the liquid.

Ideal Relativistic Bose Condensation

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The condensation temperature and the specific-heat anomaly of an ideal relativistic Bose gas are discussed. For a high concentration of bosons with small rest mass there is a marked departure from the normal nonrelativistic theory. The heat capacity C_v remains continuous at the condensation temperature unless the rest mass vanishes.

1. INTRODUCTION

ONE might expect the ideal three-dimensional relativistic Bose gas to behave near its condensation temperature in exactly the same way as the corresponding nonrelativistic gas. The lowest single-particle energy levels might be thought to play a dominant part at, and below, the condensation temperature, and under these conditions the relativistic corrections would be expected to be negligible.

This expectation is here shown to be in error. The reason can be traced ultimately to two drastic idealizations commonly adopted in this kind of theory: (i) The particles are independent, (ii) the properties of the system are considered in the limit in which the volume V and the number of particles N both tend to infinity. This usually leads to the result¹ that the

single-particle *quantum* states lying energetically above the lowest *energy* level, and extending to any finite quantum number M , play no part in the limiting properties of the system. Hence the single-particle spectrum for high quantum numbers can be important and is responsible for the differences between the relativistic and nonrelativistic cases. Along with most other exactly tractable models of phase transition, the present one is divorced from reality and should be investigated for interacting particles.

The relativistic corrections are considerable only if the rest mass of the bosons is very small, or if their concentration is very large. The bosons of smallest nonzero rest mass conceivable at present are a pair of neutrinos and a photon. If nonzero, the rest masses involved would be less than² 10^{-30} g and less than 10^{-45}

¹ P. T. Landsberg, Proc. Cambridge Phil. Soc. **50**, 65 (1954).

² P. Roman, *Theory of Elementary Particles* (North-Holland Publishing Company, Amsterdam, 1960). R. R. Lewis, Phys. Rev. **136**, B811 (1964).

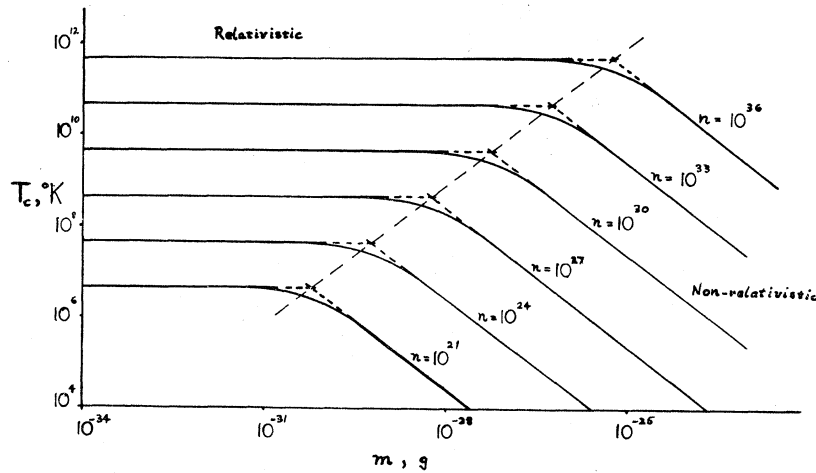


FIG. 1. The condensation temperature for an ideal relativistic Bose gas is here plotted against rest mass for various concentrations (full lines). The broken curves (----) represent the same plot for the extreme relativistic and nonrelativistic approximations, as indicated. These latter curves are shown to intersect on the straight line. (---).

g, respectively.³ Typically, departures from the non-relativistic theory occur if the rest mass is less than 3×10^{-29} g, while the concentration n exceeds 10^{24} particles per cm^3 (see Fig. 1).

2. GENERAL THEORY

Consider an ideal Bose gas with $v(E)dE$ single-particle quantum states in an energy range dE . E excludes the rest energy $\epsilon_0 \equiv mc^2$. The occupation probability of a quantum state of energy E at temperature T is

$$f(E, \alpha, T) = (e^{E/kT - \alpha} - 1)^{-1}, \quad \alpha \equiv (\mu - \epsilon_0)/kT. \quad (2.1)$$

If the number of particles in the lowest energy level is $N_1(\alpha, T)$ at temperature T , then the total number of particles in the system is

$$N - N_1(\alpha, T) = \int_0^\infty v(E) f(E, \alpha, T) dE. \quad (2.2)$$

The zero for the energy E has been chosen at that value of the lowest energy level $E = E_1$, which is found in the limit when the volume V tends to infinity. For finite volume, $\alpha < E_1/kT$; and for an infinite volume, $\alpha \leq 0$. As the temperature is lowered, the numerical value of α in the limit of infinite volume decreases, and can in some cases reach the value zero at a critical temperature $T_c > 0$. Hence for a large volume one can define this condensation temperature by

$$\alpha < 0 \text{ for } T > T_c, \quad \alpha = 0 \text{ for } T \leq T_c. \quad (2.3)$$

If (2.3) is used in (2.2), a unique condition for $T = T_c$ is not obtained unless (2.3) is supplemented by

$$N_1(\alpha, T) \ll N \text{ for } T \geq T_c, \quad (2.4)$$

where the equality sign in (2.4) is important. Below the condensation temperature, $N_1(\alpha, T)$ is a non-

negligible fraction of N . The condition for T_c is accordingly

$$N = \int_0^\infty v(E) f(E, 0, T_c) dE. \quad (2.5)$$

We have here followed a previous argument.⁴ A more rigorous foundation for these equations is possible (see Appendix).

3. THE INTEGRALS

In previous work⁵ integrals were introduced in terms of which the statistical thermodynamics of ideal relativistic quantum gases can conveniently be discussed. These are defined again on the right-hand sides of Eqs. (3.1) and (3.2), below. They are slightly modified for the present purpose:

$$K(\alpha, r, u) \equiv \int_0^\infty \frac{(x^2 + 2ux)^{1/2} (x^r + ux^{r-1})}{\exp(x - \alpha) - 1} dx \\ \equiv (kT)^{-(r+2)} K_r, \quad (3.1)$$

$$\theta(\alpha, s, u) \equiv \int_0^\infty \frac{(x^2 + 2ux)^{1/2} (x^s + ux^{s-1}) e^{x-\alpha}}{[\exp(x - \alpha) - 1]^2} dx \\ \equiv (kT)^{-(s+2)} \theta_s. \quad (3.2)$$

Here α is given by (2.1) and

$$r = 1, 2; \quad s = 1, 2, 3; \quad u \equiv \epsilon_0/kT. \quad (3.3)$$

The integrals are dimensionless and go over into multiples of the familiar integrals

$$I(\alpha, s) = \frac{1}{\Gamma(s+1)} \int_0^\infty \frac{x^s dx}{e^{x-\alpha} - 1},$$

⁴ P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations* (Interscience Publishers, Inc., New York, 1961), pp. 311-315.

⁵ P. T. Landsberg and J. Dunning-Davies, Paper presented at the International Symposium on Statistical Mechanics and Thermodynamics, Aachen, Germany, June 1964 (to be published).

³ L. de Broglie, *Mécanique Ondulatoire due Photon et Théorie Quantique des Champs* (Gauthier-Villars, Paris, 1949), p. 59.

TABLE I. Special cases of the integrals.

| | Nonrelativistic limit $u \rightarrow \infty$ | Extreme relativistic limit $u \rightarrow 0$ |
|------------------------|---|---|
| $K(\alpha, r, u)$ | $\sqrt{2}\Gamma(r+\frac{1}{2})I(\alpha, r-\frac{1}{2})u^{3/2}$ | $\Gamma(r+2)I(\alpha, r+1)$ |
| $\theta(\alpha, r, u)$ | $\sqrt{2}\Gamma(r+\frac{1}{2})I(\alpha, r-\frac{3}{2})u^{3/2}$ ($r > \frac{1}{2}$) | $\Gamma(r+2)I(\alpha, r)$ ($r > -1$) |

as shown in Table I. If $\zeta(s)$ denotes the Riemann zeta function; we also have

$$I(0, s) = \zeta(s+1), \quad (s > 0). \tag{3.4}$$

4. THE CONDENSATION TEMPERATURES

Taking account of a spin degeneracy ω , the required density of states is

$$v(E) = (4\pi\omega V/h^3c^3)(E + \epsilon_0)(E^2 + 2\epsilon_0E)^{1/2}. \tag{4.1}$$

Inserting (4.1) and (2.1) into (2.2) to (2.5), and using (3.1) and (3.2) one finds, for example, from (2.2)

$$N - N_1(\alpha, T) = 4\pi\omega V(kT/hc)^3 K(\alpha, 1, u), \quad (\text{all } T). \tag{4.2}$$

Equation (2.5) yields the relation for T_c

$$N = 4\pi\omega V(kT_c/hc)^3 K(0, 1, u_c), \tag{4.3}$$

where

$$u_c = mc^2/kT_c. \tag{4.4}$$

The condensation temperature is seen to depend only on the particle density $n = N/V$ and the rest mass m . It can be computed from (4.3) (see Fig. 1).⁶

To obtain approximate solutions of (4.3) one can expand the numerator of the integrand of $K(0, 1, u_c)$ binomially to find

$$\begin{aligned} K(0, 1, u_c) &= (\pi u_c/2)^{1/2} [\zeta(3/2)u_c + (15/8)\zeta(5/2)], \\ &\hspace{15em} (u_c \gg 1) \\ &= 2\zeta(3) + 2\zeta(2)u_c, \hspace{15em} (u_c \ll 1). \end{aligned}$$

These approximations correspond to the nonrelativistic and extreme-relativistic cases. The corresponding lines are seen from the figure to intersect on a further straight line. If m is in grams, its equation is

$$T_c = \frac{mc^2}{2k} \left\{ \pi \left[\frac{\zeta(\frac{3}{2})}{\zeta(3)} \right]^2 \right\}^{1/3} = 8 \times 10^{36} m \quad (\text{°K}).$$

Relativistic effects are important above this line, i.e., for very small rest masses: The higher the concentration the higher the rest mass at which the effects begin to appear.

In the two limiting cases of Table I, (4.3) yields

$$kT_c = \frac{h^2}{2\pi m} \left[\frac{N}{\omega V \zeta(\frac{3}{2})} \right]^{2/3} \quad (\text{nonrelativistic}) \tag{4.5}$$

$$= \left[\frac{h^3 c^3 N}{8\pi\omega V \zeta(3)} \right]^{1/3} \quad (\text{extreme relativistic}). \tag{4.6}$$

⁶ We are indebted to Dr. P. Lal of this department for assistance with the computation.

Equation (4.5) is a familiar result for a nonrelativistic three-dimensional gas of bosons. More generally, for a nonrelativistic gas of bosons having a density of states

$$v(E) = AE^s \quad (s > -1), \tag{4.7}$$

where A is proportional to volume, one finds

$$kT_c = \left[\frac{N}{A\Gamma(s+1)\zeta(s+1)} \right]^{1/(s+1)}. \tag{4.8}$$

(4.5) and (4.6) are special cases of this result which occur if $s = \frac{1}{2}$ and $s = 2$, respectively. A condensation temperature $T_c > 0$ exists in this case if $s > 0$. It is associated with a discontinuity in the derivative of the heat capacity C_v if $s \geq \frac{1}{2}$, and with a discontinuity in C_v itself if $s > 1$.⁴ Hence, in the case of the relativistic gas one might expect (i) that a condensation temperature $T_c > 0$ exists always, (ii) that a discontinuity in the heat capacity C_v develops as soon as one leaves the nonrelativistic limit, and (iii) that this discontinuity becomes more pronounced as the relativistic region is approached. It will be seen in the next section that only (i) is correct, whereas (ii) and (iii) are incorrect.

The two temperatures, (4.5) and (4.6), are related as follows

$$\frac{(T_c)_{nr}}{(T_c)_{er}} = C \left(\frac{N\lambda^3}{\omega v} \right)^{1/3}, \tag{4.9}$$

where

$$C = \left[\frac{8\pi\zeta(3)}{[\zeta(\frac{3}{2})]^2} \right]^{1/3} = 1.643 \tag{4.10}$$

and $\lambda \equiv \hbar/mc$ is the Compton wavelength of the particle.

5. THE ANOMALIES IN C_v

It is known⁵ that the heat capacity at constant volume of an ideal relativistic gas of bosons is

$$\begin{aligned} C_v &= 4\pi\omega V k \left(\frac{kT}{hc} \right)^3 \left\{ \theta(\alpha, 3, u) - \frac{\theta^2(\alpha, 2, u)}{\theta(\alpha, 1, u)} \right\} \\ &\hspace{15em} (T > T_c) \\ &= 4\pi\omega V k \left(\frac{kT}{hc} \right)^3 \theta(0, 3, u), \hspace{15em} (T < T_c). \end{aligned} \tag{5.1}$$

A term due to $(\partial\alpha/\partial T)_v$ contributes to the first expression. The second expression is simpler because this term vanishes for $T < T_c$. Alternatively, introducing (4.2) or (4.3) into (5.1),

$$\begin{aligned} C_v &= \frac{Nk}{K(\alpha, 1, u)} \left\{ \theta(\alpha, 3, u) - \frac{\theta^2(\alpha, 2, u)}{\theta(\alpha, 1, u)} \right\} \quad (T > T_c) \\ &= Nk \left(\frac{T}{T_c} \right)^3 \frac{\theta(0, 3, u)}{K(0, 1, u_c)}, \hspace{15em} (T < T_c). \end{aligned} \tag{5.2}$$

The discontinuity in C_v at $T=T_c$ is accordingly

$$\Delta = (C_v)_{T_c-} - (C_v)_{T_c+} = Nk \frac{\theta^2(0,2,u_c)}{\theta(0,1,u_c)K(0,1,u_c)}. \quad (5.3)$$

Thus using Table I and Eq. (3.4)

$$\Delta = 0 \quad (u_c \neq 0) \quad (5.4)$$

$$= 9Nk\zeta(3)/\zeta(2) = 6.576Nk \quad (u_c = 0). \quad (5.5)$$

The fact that $\theta(\alpha,1,u_c) \rightarrow \infty$ as $\alpha \rightarrow 0$ for $u_c \neq 0$ has here been used. There is no break in C_v unless the rest mass is zero.

The anomaly Δ has therefore the same values as are obtained by a nonrelativistic theory based on (4.7)¹ with

$$s = \frac{1}{2} \text{ for Eq. (5.4) and } s = 2 \text{ for Eq. (5.5).} \quad (5.6)$$

The result (5.5) has recently been discussed in a different context.⁷

APPENDIX: MORE RIGOROUS DERIVATION OF THE MAIN EQUATIONS

The known argument for a reasonably rigorous discussion of Bose condensation may be extended to the relativistic gas as follows. (For more details the original reference⁸ should be consulted.) Make the following assumptions: (i) An infinity of single-particle quantum states $1, 2, \dots, j, \dots$ of energies $E_1 \leq E_2 \leq \dots$ exist. E_j is finite if j is finite and tends to energy $E_0 = 0$ as $V \rightarrow \infty$. (ii) For large volumes V , and if σ, τ, a , and d are constants, there exists an integer M_0 such that for $j \geq M_0$ a continuous spectrum approximation can be made with E_j given by

$$(E_j + a)^\sigma = a^\sigma + d(j/v)^\tau. \quad (A1)$$

Equivalently, the density of states

$$v(E) = (\sigma/\tau) V d^{-1/\tau} [(E_j + a)^\sigma - a^\sigma]^{1/\tau-1} [E_j + a]^{-\sigma-1} \quad (A2)$$

may be specified.

Table II shows that these expressions cover the nonrelativistic limit as well as the relativistic situation. The parameters d and τ could be kept general, but for convenience the table includes appropriate values for a three-dimensional gas.

TABLE II. Interpretation of constants in Eqs. (A1) and (A2).

| | a | σ | τ | d |
|-----------------------|---------------------|----------|---------------|--|
| Nonrelativistic limit | 0 | 1 | $\frac{2}{3}$ | $\frac{h^2}{2\pi m} [\Gamma(\frac{3}{2})]^{2/3}$ |
| Relativistic theory | $\epsilon_0 = mc^2$ | 2 | $\frac{2}{3}$ | $h^2 c^2 (3/4\pi\omega)^{2/3}$ |

¹ R. M. May, Phys. Rev. 135, A1515 (1964).

⁸ Reference 4, Appendix D.

Consider a property F such that $F(j)$ is the contribution made to F by a particle in quantum state j . Then, assuming the infinite sum to converge, and $F(j)$ to be finite for finite j , the mean value of F is given by

$$\frac{\bar{F}}{V} = \frac{g_1}{V} \frac{F(1)}{e^{\eta_1 - \alpha} - 1} = \sum_{j=g_1+1}^{\infty} \frac{F(j)/V}{e^{\eta_j - \alpha} - 1}, \quad \eta_j = \frac{E_j}{kT}. \quad (A3)$$

Here g_1 is the degeneracy of the lowest energy level and α is defined in (2.1). For a Bose gas, $\alpha \leq \eta_1$, so that

$$(\eta_j - \alpha)^{-1} \leq (\eta_j - \eta_1)^{-1}. \quad (A4)$$

Take any term with finite j on the right-hand side of (A3) as $V \rightarrow \infty$, $\eta_j \rightarrow \eta_0 = 0$, and there exists a δ such that $\alpha \rightarrow \eta_1 - \delta = -\delta$. If $\delta > 0$ a term with finite j in (A3) clearly goes to zero as $V \rightarrow \infty$. If $\delta = 0$, one is at or below the condensation temperature, and for large enough volumes a typical term satisfies, by (A1) and (A4), the expression

$$\frac{F(j)/V}{e^{\eta_j - \alpha} - 1} = \frac{F(j)}{V} \frac{1}{\eta_j - \alpha} \leq \frac{F(j)}{V(\eta_j - \eta_1)} = \frac{F(j)kT}{V} \frac{1}{[a^\sigma + d(j/v)^\tau]^{1/\sigma} - [a^\sigma + d(v^{-\tau})]^{1/\sigma}}. \quad (A5)$$

When $a = 0$, this expression tends to zero for $\tau < \sigma$, while, when $a \neq 0$, a value of V can always be found such that the denominator may be expanded and then the expression tends to zero for $\tau < 1$. Hence any finite number of terms having finite j can be omitted from the right-hand side of (A3) for large enough volumes, provided only τ is smaller than 1 and σ . Omitting all states from $j = g_1 + 1$ to $j = M \geq M_0$ one can now use assumption (ii) to find for large enough V

$$\frac{\bar{F}}{V} = \frac{g_1}{V} \frac{F(1)}{e^{\eta_1 - \alpha} - 1} = \frac{1}{V} \int_0^\infty \frac{v(E)F(E)}{e^{E/kT} - 1} dE. \quad (A6)$$

If $F(j) = 1$, \bar{F} is the mean number of particles in the system, and (A6) yields (2.2).

For large enough volumes (A3) (with the states for which j satisfies $g_1 + 1 \leq j < M$ omitted) also yields

$$\left[\frac{\bar{F}}{V} - \sum_{j=M}^{\infty} \frac{F(j)/V}{e^{\eta_j - \alpha} - 1} \right] [e^{\eta_1 - \alpha} - 1] = 0, \quad (M \geq M_0). \quad (A7)$$

In the limit $V \rightarrow \infty$, $\alpha \rightarrow -\delta$. If $\delta > 0$, the first factor vanishes; if $\delta = 0$, the second factor vanishes. The transition, if present, occurs at the condensation temperature T_c when both factors vanish. Thus T_c is given by

$$\frac{\bar{F}}{V} = \sum_{j=M}^{\infty} \frac{F(j)/V}{e^{E/kT_c} - 1}.$$

This yields Eq. (2.5) if $F(j) = 1$.