

TABLE I. *L* (g-cal./mole) Comparison of results of present theory with those of Bleaney and Simon.

Temp. °K	Bleaney Simon	Eq. (7)
1.4	—	20.49
1.2	—	19.98
1.0	19.18	19.13
0.8	18.21	18.21
0.6	17.22	17.24
0.4	16.23	16.24
0.2	15.24	15.25
0.1	14.75	14.75
0.01	14.31	14.31
0.00	14.26	14.257

which, respectively, are the vapor volume and the liquid volume of the saturated fluid, we get for the difference of the roots

$$v_v - v_l = \left[ \left( \frac{RT}{2p} \right)^2 - \frac{A}{pT} \right]^{\frac{1}{2}}. \quad (2)$$

The constant  $A$  is evaluated from Eq. (2), noting that at the critical point,  $v_v - v_l = 0$ .

Thus

$$A = R^2 T_c^3 / 4 p_c.$$

Subscripts  $c$  indicate critical values.

Then

$$v_v - v_l = \frac{R}{p} \left( T^2 - \frac{Dp}{T} \right)^{\frac{1}{2}} \quad \text{where} \quad D = \frac{T_c^3}{p_c}. \quad (3)$$

From the Clapeyron-Clausius equation,

$$L = dp/dT(v_v - v_l),$$

and Eq. (3) we obtain for the heat of vaporization, per mole

$$L = R \frac{dp}{dT} \frac{T}{p} \left( T^2 - \frac{Dp}{T} \right)^{\frac{1}{2}}. \quad (4)$$

The vapor pressure of saturated helium II, below 1.5°K, is given by the expression<sup>2</sup>

$$\log p_{\text{atmos}} = -\frac{3.117}{T} + 2.5 \log T - 0.6848. \quad (5)$$

Then

$$\frac{dp}{dT} = \left( \frac{7.1775}{T} + 2.5 \right) \frac{p}{T}. \quad (6)$$

Taking  $p$  in atmos.,  $T$  in °K, ice point = 273.16°K,  $p_c = 2.261$  atmos.,  $T_c = 5.25$ °K,  $R = 0.08206$ , and 1 liter-atmos. = 24.206 g-cal.; we obtain for Eq. (4)

$$L = \left( \frac{14.257}{T} + 4.9659 \right) \left( T^2 - \frac{Dp}{T} \right)^{\frac{1}{2}}. \quad (7)$$

Below 0.6°K, since  $T \gg Dp/T$ , Eq. (7) reduces to

$$L = 14.257 + 4.966T. \quad (8)$$

Bleaney and Simon<sup>3</sup> have calculated the heat of vaporization of helium, up to 1°K, from entropy considerations. Their values and the figures given by Eq. (7) are compared in Table I.

<sup>1</sup> J. E. Haggemacher, *J. Am. Chem. Soc.* **66**, 313 (1944).

<sup>2</sup> Burton, Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 69.

<sup>3</sup> Bleaney and Simon, *Trans. Faraday Soc.* **35**, 1205 (1939).

### Bose-Einstein Condensation of Trapped Electron Pairs. Phase Separation and Superconductivity of Metal-Ammonia Solutions

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WITH the invaluable assistance of Drs. Claudio Alvarez-Tostado and William Perkins, the previously reported<sup>1</sup> studies of the behavior resulting from rapid freezing of very dilute solutions of alkali metals in liquid ammonia have been extended (in the case of sodium solutions) over the entire concentration range, up to the saturation point. Sufficiently rapid cooling to temperatures in the range from  $-90^\circ\text{C}$  to  $-180^\circ\text{C}$  resulted in the production of apparently homogeneous deep-blue solid solutions, of bronze-like luster when extremely concentrated. All of the solid samples proved to be good electrical conductors, although shrinkage and cracking frequently caused erratic measurements. No abnormal resistance change accompanying solidification was observed, except for solutions in the concentration range (of the order of one molar) characterized by the remarkable phenomenon of separation into two dilute liquid phases<sup>2</sup> at sufficiently low temperatures. Extremely rapid freezing of such solutions (initially at  $-33^\circ\text{C}$ , i.e., above the upper consolute temperature) caused a relatively enormous decrease of measured resistance. In a representative case, the resistance of the liquid sample at  $-33^\circ\text{C}$  was some 10,000 ohms, while that of the solid at  $-95^\circ\text{C}$  was only 16 ohms. Variation of conditions suggested that even such small residual resistances might be due to "end effects" and faulty contact with the platinum electrodes. That the solutions in this special concentration range actually became superconducting was demonstrated by adaptation of the classical Kammerlingh Onnes "ring experiment." Thin-walled glass cells having the shape of an annular disk were filled with the proper solution at  $-33^\circ\text{C}$  and then rapidly plunged into a vessel of liquid air between the poles of an electromagnet (field strength some 1500 gauss). After removal from the magnetic field, the existence of persistent currents was shown by tests with a sensitive magnetometer. Numerous control experiments obviated any other possible explanation. The magnetometer tests were conducted at  $-180^\circ\text{C}$ , but intervening warming of the ring samples to much higher temperatures did not destroy the persistent currents. In all probability such solid solutions remain superconducting up to the melting point, i.e., to absolute temperatures of the order of 180 to 190 degrees.

The probable explanation of the above phenomena is to be found in the behavior of trapped electron pairs, recently demonstrated<sup>3</sup> to be a stable constituent of fairly dilute metal-ammonia solutions. In the concentration range characterized by liquid-liquid phase separation, experimental studies<sup>4</sup> show the solute to be diamagnetic at temperatures just above the consolute point. This suggests the electron constituent to be almost exclusively in the trapped electron pair configuration. Because of their

zero angular momentum, such pairs must obey Bose-Einstein statistics. If the effective mass does not exceed twice the electron mass by an extremely large factor, then the calculated degeneration temperature<sup>5</sup> at the concentrations in question is relatively high—of the order of a few hundred degrees absolute. It is postulated that the liquid-liquid phase separation which occurs on slow cooling (upper consolute temperature 232°K) is the device adopted by the systems to avoid the Bose-Einstein condensation, with its unfavorable free energy change. In the more dilute phase the electron constituent is still predominantly the trapped pair, but at a concentration low enough to raise the degeneracy temperature to just above the prevailing temperature. In the more concentrated phase, the trapped electron pairs have become unstable because of the greater interionic forces, and one has essentially a liquid metal, the trapped single electrons being below the Fermi-Dirac degeneration temperature. The small, temperature independent paramagnetism<sup>4</sup> of very concentrated solutions would appear to support this latter model.

By sufficiently rapid cooling, it appears that the liquid-liquid phase separation is prevented, and that the system becomes frozen and hence metastable in the "forbidden" concentration region, which is thus characterized by the Bose-Einstein condensation of trapped electron pairs. From the discussion of London,<sup>5</sup> apparently such a state must display the phenomenon of electrical superconductivity, in agreement with the above experimental observations.

The extension of the above model to explain previously observed superconductivity is apparent, and is the more plausible in view of the essentially only quasi-metallic character of the large number of alloys and compounds which display the phenomenon.<sup>6</sup>

<sup>1</sup> R. A. Ogg, Jr., *J. Chem. Phys.* **13**, 533 (1945).

<sup>2</sup> For literature references, see W. C. Johnson and A. W. Meyer, *Chem. Rev.* **8**, 273 (1931).

<sup>3</sup> R. A. Ogg, Jr., *J. Chem. Phys.* **14**, 114 (1946).

<sup>4</sup> E. Huster, *Ann. d. Physik* [5], **33**, 477 (1938); S. Freed and N. Sugarman, *J. Chem. Phys.* **11**, 354 (1943).

<sup>5</sup> F. London, *Phys. Rev.* **54**, 947 (1938).

<sup>6</sup> H. G. Smith and J. V. Wilhelm, *Rev. Mod. Phys.* **7**, 237 (1935).

### Concerning Some New Methods of Acceleration of Relativistic Particles

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IN two papers<sup>1,2</sup> appearing in 1944 under the above title the author of the present letter pointed out two new principles of acceleration of relativistic particles which generalize the resonance method.

New possibilities for the resonance acceleration of particles in a constant magnetic field are described in the first of these papers, and the possibility of resonance acceleration in magnetic fields which increase with time is also noted.

This latter case is specially examined in the second paper. It is shown that phase stability automatically sets in if

the time variation of the field is sufficiently small; relation between the amplitude of the variable electric fields and the rate of variation of the magnetic field is established.

It is also pointed out that the radiation losses in such acceleration do not violate phasing mechanism. Finally in a detailed paper<sup>3</sup> an accelerator of heavy particles based on a variation in frequency is analyzed.

Thus the foregoing papers cover completely the contents of the note by McMillan<sup>4</sup> in which no reference is made to my investigations.

Construction of a 30-Mev accelerator with varying magnetic field is now nearing completion at the Physical Institute of the Academy of Sciences, U.S.S.R.

<sup>1</sup> V. Veksler, *Comptes Rendus (Doklady), Acad. Sci. U.S.S.R.* **43**, No. 8, 444 IX (1944) (communicated April 25, 1944).

<sup>2</sup> V. Veksler, *Comptes Rendus (Doklady), Acad. Sci. U.S.S.R.* **44**, No. 9, 393 (1944) (communicated July 19, 1944).

<sup>3</sup> V. Veksler, *J. Phys. (U.S.S.R.)* **9**, No. 3, 153 (1945) (received March 1, 1945).

<sup>4</sup> E. McMillan, *Phys. Rev.* **68**, 143 (1945).

### Erratum: A Method for Measuring Effective Contact e.m.f. between a Metal and a Semi-Conductor

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[*Phys. Rev.* **69**, 42 (1946)]

UNFORTUNATELY Fig. 1 which should have appeared with the above Letter to the Editor was omitted. It is reproduced here.

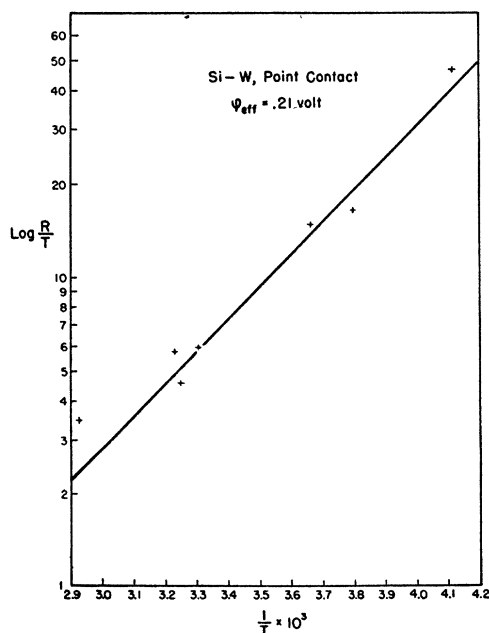


FIG. 1