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- ¹D. G. Wickham and W. J. Croft, J. Phys. Chem. Solids 7, 351 (1958).
- ²B. Boucher, R. Buhl, and M. Perrin, J. Appl. Phys. **39**, 632 (1968).
- ³D. E. Cox, Int. J. Magn. 6, 67 (1974); reprinted inMagnetoelectric Interaction Phenomena in Crystals (ed. A. J. Freeman and H. Schmid), Gordon and Breach, 1975, p. 111.

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Experimental investigation of the phase transition to the superfluid state in helium located in narrow pores

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The phase transition to the superfluid state of helium contained in narrow pores with dimensions of 100-600 Å has been investigated by the calorimetric method. Singularities typical of a first-order phase transition are observed for helium in narrow pores (100-200 Å). The parameter M in the ψ theory of superfluidity and the coefficients A_0 , B_0 and C_0 in the three-term expansion of the thermodynamic potential are estimated. The latent heat of the transition and its dependence on the pore size are determined.

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1. In the phenomenological theory of superfluidity (the ψ theory),¹⁻³ the expansion of the thermodynamic potential in a power series in the order parameter has the form

$$\Phi_{II} = \Phi_{I} + A |\psi|^{2} + \frac{1}{2} B |\psi|^{4} + \frac{1}{3} C |\psi|^{4} \dots, \qquad (1)$$

where Φ_{I} and Φ_{II} are the thermodynamic potentials of homogeneous, stationary He-I and He-II near the λ point, and A, B, C are expansion coefficients, which are temperature dependent. In a modified variant of the ψ theory,

$$A = -A_{0}(T_{\lambda} - T) |T_{\lambda} - T|^{\frac{1}{3}}, \quad B = B_{0} |T_{\lambda} - T|^{\frac{2}{3}}, \quad C = C_{0}.$$
(2)

Under conditions in which coefficients of type (2) are used, all the terms in (1) that are proportional to $|\psi|^2$, $|\psi|^4$, $|\psi|^6$, depend in the same manner on $T_{\lambda} - T$ at equilibrium, and there is no basis for discarding terms of higher order in $|\psi|^2$ as $T \rightarrow T_{\lambda}$. However, in narrow pores, where the equilibrium value of the density of the superfluid component ρ is less than the corresponding equilibrium value of for the bulk immobile He-II, the discarding of terms with $|\psi|^8$ and higher is already valid.

In the three-term expansion (1), two restrictions can be placed on the coefficients A_0 , B_0 , C_0 (2) by requiring that they furnish the correct experimental value of the jump in the specific heat in the free (bulk) liquid Δc_{μ} = 5.2 × 10⁷ erg/g-deg, and the value of the coefficient in the temperature dependence of ρ_{se} :

$$\rho_{se} = 1.43 \rho_{\lambda} (T_{\lambda} - T)^{\frac{\gamma_{1}}{2}} = \rho_{00} (T_{\lambda} - T)^{\frac{\gamma_{1}}{2}}.$$

Introducing the dimensionless variable $\varphi = \psi/\psi_0$, where $\psi_0 = (\rho_0/m)^{1/2}$, and the relative temperature $t = T_{\lambda} - T$, we obtain

$$\Phi_{11}-\Phi_{1}=\frac{3\Delta c_{b}}{(3+M)T_{\lambda}}\left(-t|t|^{\gamma_{b}}|\phi|^{2}+\frac{1}{2}(1-M)|t|^{\gamma_{b}}|\phi|^{4}+\frac{1}{3}M|\phi|^{4}\right),$$
(3)

where $M = C_0 \psi_0^4 / A_0$ is a dimensionless parameter. Comparison of (3) with (1) gives

$$A_{0} = \frac{3\Delta c_{b}}{(3+M)T_{\lambda}\psi_{00}^{2}}, \quad B_{0} = \frac{3(1-M)\Delta c_{b}}{(3+M)T_{\lambda}\psi_{00}^{4}}, \quad C_{0} = \frac{3M\Delta c_{b}}{(3+M)T_{\lambda}\psi_{00}^{4}}.$$
(4)

The parameter M is not determined within the framework of the phenomenological theory and must be estimated from experiment. It is shown in the ψ theory³ that the value of the parameter M determines the type of the phase transition to the superfluid state: for M<1 this transition should be second order, while for M > 1, it should be first order.

The aim of the present work is the experimental investigation of the character of the phase transition to the superfluid state of helium contained in narrow pores, by the calorimeteric method, and the determination, on the basis of experimental data, of the parameter M and of the coefficients A_0 , B_0 , C_0 of the three-term expansion of the thermodynamic potential in a power series in the order parameter.

2. The method of measurement consists in the following: Heat is released at a given rate by a thermally isolated sample and the time dependence of the temperature in it is investigated.

The calorimeter was a Dewar with a volume of 10 cm³, sealed with a ground stopper with a small aperture and provided with a guard ring preventing flow of the film. A porous medium was created in the calorimeter by filling it with powders chosen with the help of an electron microscope JM-50; the powder filling had pores with mean characteristic dimensions 100, 200, 300, 500 and 600 Å, respectively. An Allen-Bradley resistance thermometer was placed at the center of the medium. The calorimeter was suspended from a lifting mechanism. After filling, the calorimeter with the helium-II was raised slightly, thus cutting off a certain mass m_{b} of helium contained in the pores from the bath. Further, by shutting off the pumping of the bath vapor. self-heating of the helium took place in the pores, always at a definite level of the helium in the bath and at a definite location of the calorimeter relative to the level in the bath. This assured identical rates of entrance of the heat into the calorimeter in all the experiments. For comparison, a thermogram was prepared at the same time for the helium contained in an identically located calorimeter, the same as the first, but without the powder (i.e., in a free volume of the helium).

3. The thermograms taken for helium contained in 500 and 600 Å pores did not reveal any singularities, within the limits of experimental error, in comparison with the helium in the free volume. The thermograms taken for helium in the 100, 200, and 300 Å pores are shown in Fig. 1.⁴ Along with the shift in the λ point, it was observed that at the time of the transition the temperature of the helium did not change, in spite of the continuous heat intake from the outside (the region of the plateau in Fig. 1), while the time duration of the plateau τ was greater, the smaller the dimensions of the pores. Such a behavior is typical of a first-order phase transition associated with the absorption of latent heat. We note that the observed singularities are not connected with the thermal properties of the powders.

Estimates show that the heat capacity of the powder is smaller by a factor of 10^5 than the heat capacity of the helium in the calorimeter. Moreover, a control experiment, in which thermograms from two thermometers, located in different parts of the calorimeter and recorded simultaneously on two recorders, showed that the transition occurs simultaneously at both points,



FIG. 1. Thermograms taken for helium in pores with mean characteristic dimensions of 100, 200, 300 Å and in a free volume (read the curves in order from bottom to top).

and consequently is not connected with the thermal conductivity of the powder material.

The experimental values obtained for the shift in the λ point do not permit a determination of the parameter M, since, first, the value of the shift depends weakly on the value of M,³ and second, the determination of M from the shift in the λ point requires the presence of exactly determined pore dimensions. In our experiment, however each porous sample has its own pore size distribution function, which makes difficult the quantitative comparison of the experimental results with the ψ theory. It has not yet been possible to overcome this difficulty in any of the experiments known to us.

Nevertheless, the experimental data do allow a determination of the parameter M indirectly, through the quantity $k = \overline{\Delta} c_p/c_M$ (where $\overline{\Delta} c_p$ and Δc_M are the jumps in the heat capacities at the point of transition in the pores and in the free volume, respectively),⁵ since the change in the parameter M for thin films most strongly affects the value of k (see Table III in the work of Ginzburg and Sobyanin³). The function k(M), plotted on the basis of the Table mentioned, is shown in Fig. 2.

The value of k is determined from the experiments in the following way. As was pointed out above, in the self-heating of the helium, the rate of heat release in the calorimeter is the same for a calorimeter without the powder and with one, i.e.,

$$c_{\mathbf{M}}m_{\mathbf{M}}\left(\frac{dT}{dt}\right)_{\mathbf{M}}=\bar{c}_{p}m_{p}\left(\frac{dT}{dt}\right)_{p},$$

where c_M , m_M , $(dT/dt)_M$ are respectively the heat capacity, the mass, and the rate of change of the temperature for free helium in the calorimeter without the powder, while \overline{c}_p , m_p , $(dT/dt)_p$ are the same quantities for helium in the pores, and $\overline{c}_p = c_I + k \Delta c_M$ where c_I is the specific heat of He-I. Thus, we obtain for k

$$k = \frac{1}{\Delta c_{\mathrm{M}}} \left[c_{\mathrm{M}} \frac{m_{\mathrm{M}}}{m_{p}} \frac{(dT/dt)_{\mathrm{M}}}{(dT/dt)_{p}} - c_{\mathrm{I}} \right].$$

In this formula, $\Delta c_{\mu} = 5.2 \times 10^7$ erg/g-deg, $c_{\rm I}$ and c_{μ} are calculated from the known empirical formulas

 $c_{1} = -0.65 - 3.00 \, \lg |T_{\lambda} - T| [J/g \cdot \deg],$ $c_{\mu} = 4.55 - 3.00 \, \lg |T_{\lambda} - T| [J/g \cdot \deg],$

 $(dT/dt)_{\mu}$, $(dT/dt)_{\rho}$ are taken from the thermograms. The ratio of the masses was estimated in a separate experiment, in which the calorimeter was suspended



FIG. 2. Dependence of k(M) constructed on the basis of the data of Table III in Ref. 3.



FIG. 3. Dependence of the latent heat of transition L (in units of J/g) on the mean characteristic size of the pores d (in Å) in log-log scale.

from an elastic filament:

$$\frac{m_p}{m_{\rm M}} = \frac{I_p}{I_{\rm M}} = \frac{\theta^3 - \theta_0^2}{\theta_2^2 - \theta_1^2},$$

here θ_0 and θ are the periods of oscillation of the calorimeter with powder in a vacuum and with helium-II near the λ point, θ_1 and θ_2 are the same quantities for the calorimeter without the powder, I_p and I_M are the moments of inertia of the helium contained in the pores and in free volume, respectively. Measurements have shown that for all the samples $m_p/m_M = 0.60 \pm 0.02$. According to estimates, the pores with dimensions 100-300 Å can be assumed to be narrow in the range $T_{\lambda} - T < 10^{-2}$ K.

Substitution of all the calculated quantities in (5) gives the value $k = 3.0 \pm 0.6$. According to Fig. 2, this value of the quantity k corresponds to $M = 1.7 \pm 0.2$. Thus, the experimental data confirm the conclusion of the theory that at M > 1 the phase transition to the superfluid state in narrow pores is a first order transition.

From the experimental data, we estimated the latent heat of the transition⁴

$$L = \frac{m_{\rm M}}{m_p} c_{\rm M} \left(\frac{dT}{dt}\right)_{\rm M} \tau.$$

Figure 3 shows the dependence of L on the average characteristic size of the pores d on a log-log scale, from which it follows that $L \sim d^{-3/2}$.

The value of the parameter M that we have obtained permits us to estimate the coefficients of (4):

$$\begin{split} A_{0} &= (7.1 \pm 0.3) \cdot 10^{-17} \ \text{erg/deg}^{4/3} , \\ B_{0} &= -(1.6 \pm 0.4) \cdot 10^{-39} \ \text{erg/cm}^{3} \cdot \text{deg}^{2/3} , \\ C_{0} &= (1.2 \pm 0.1) \cdot 10^{-61} \ \text{erg/scm}^{6} . \end{split}$$

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- ¹V. L. Ginzburg and L. P. Pitaevskii, Zh. Eksp. Teor. Fiz. **34**, 1240 (1958) [Sov. Phys. JETP **7**, 858 (1958)].
- ²Yu. G. Mamaladze, Zh. Eksp. Teor. Fiz. 52, 729 (1967) [Sov. Phys. JETP 25, 479 (1967)].
- ³V. L. Ginzburg and A. A. Sobyanin, Usp. Fiz. Nauk **120**, 153 (1976) [Sov. Phys. Uspekhi **19**, 773 (1976)].
- ⁴G. A. Gamtsemlidze, D. N. Tsaava, G. K. Shoniya and S. el-Sabban, Soobshcheniya AN GSSR 95, 69 (1979).

⁵G. A. Gamtsemlidze, D. N. Tsaava, G. K. Shoniya and S. el-Sabban, Soobshcheniya AN GSSR 98, 569 (1980).

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