

fore we conclude that there are no experimental results which must

ious isotherms yield and these values are parameters of a logarithmic singularity which our calculations to 1 atm on each side indicated that there is a discontinuity at these points. This is the calculation which appears as a small change in the data. Difficulties arise in the data obtained very good agreement near the melting transition he presents for the data obtained are increasing in regularity. Grilly<sup>18</sup> has calculated at a number of points not present these values we have been able to fit his data. Fig. 11, and considering the fact that the

comparison had to be rather indirect, we find that the agreement is excellent.

It is also possible to calculate the isothermal compressibility from our expansion-coefficient data by using the thermodynamic relation

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_t - \left(\frac{\partial P}{\partial T}\right)_t V k_T. \quad (8)$$

We have calculated  $k_T$  from this expression for the region  $10^{-3} < |P - P_\lambda| < 1$  atm by using the cylindrical approximation<sup>26</sup> and these points are also shown in Fig. 11. It is apparent that while the new intercept parameters are in good agreement with the other values, the slope parameters are not. In particular the cylindrical approximation indicates that the two logarithmic branches are close to being parallel. This is the consequence of the two branches of  $\alpha_P$  being nearly parallel and the form of the approximation used. Since there is this disagreement we conclude that the conditions required for the cylindrical approximation to be valid have not been fulfilled. It should be noted that according to our first calculations,  $A_{II}''$  is greater than zero at low pressures. This means only that the minimum in  $k_T$  along the isobars is closer to the transition than  $10^{-3}$  atm. Thus the limiting form of the compressibility has not been reached and the cylindrical approximation can not be valid under these conditions.

Some of the anomalies of certain properties are shown in Fig. 12. The  $k_T$  minima along the isotherms and along the isobars and the minima of the isobaric molar volume are presented in a  $P$ - $T$  diagram. The locus of  $\alpha_P=0$  is also the locus of entropy maxima, in virtue of a Maxwell relation. It is interesting to note the gradual widening of the separation of the curves from the  $\lambda$  line as the pressure increases. The  $\alpha_P=0$  curve becomes roughly parallel to the  $\lambda$  line above about 20 atm.

#### IV. CONCLUSION

We have presented and examined molar volume data for liquid He<sup>4</sup> and have used them to calculate various

<sup>26</sup> A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, England, 1957), Chap. IX.

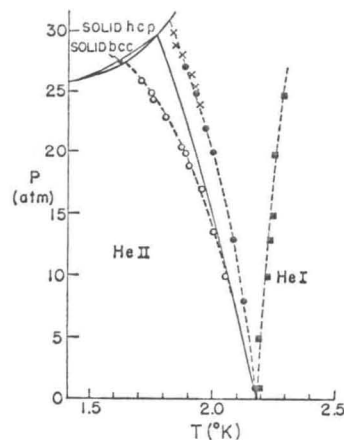
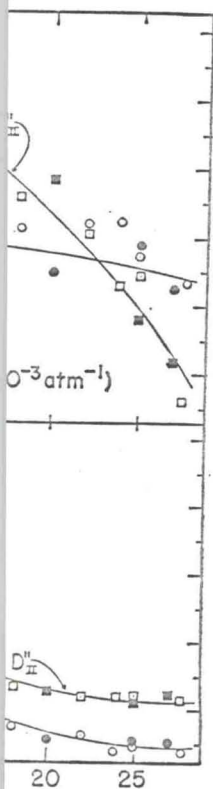


FIG. 12. The  $P$ - $T$  phase diagram of He<sup>4</sup> close to the  $\lambda$  line. Black circles: locus of  $\alpha_P=0$  (present results); X: locus of  $\alpha_P=0$  [Grilly and Mills (Ref. 5)]. Open circles:  $k_T$  minima along the isotherms [Grilly (Ref. 18)]. Black squares:  $k_T$  minima along the isobars (present results). Solid line:  $\lambda$  line

other thermodynamic properties of the fluid. In particular we have made a detailed study of the isobaric coefficient of thermal expansion to within about  $2.10 \times 10^{-5}$  K of the  $\lambda$  line. This coefficient can be represented for all pressures in terms of a logarithmic singularity which becomes steeper as the pressure is increased. This conclusion is reached at least for the interval  $10^{-2} \geq |T - T_\lambda| \geq 2 \times 10^{-5}$ . The derivative  $(\partial P / \partial T)_V$  can also be expressed in terms of a logarithmic singularity over this range of  $|T - T_\lambda|$ , although it is clear that this relationship cannot hold at the  $\lambda$  line. The derivatives  $(\partial P / \partial T)_V$  as well as  $k_T$  are in agreement with all available direct measurements. On the other hand, we have attempted to use the cylindrical approximation for calculating  $k_T$  and have found that it does not give satisfactory results over the range of temperature displacement down to  $10^{-5}$  K.

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in  $\text{atm}^{-1}$ ) for the logarithmic squares are for  $T < T_\lambda$ . Calculations from experimental data using the cylindrical approximation (Ref. 18).