ORDER-DISORDER PHENOMENA. I

L aspects of the I. In this case, e Ising pressure if J and $dJ/d\sigma$ simply related 69 kT_c) and it $dJ/d\sigma < 0$. Let ere n is a small pical disorderedr a small range

(11)

ds.

ire

an external ap $p_{dl} = p_{dl} + p_I$. We nal pressure, for of p_I and $-p_{dI}$ $T_2 < \cdots T_6 < T_7$ e isotherms will sternal pressure fied (that is, if at of p_I). Now $p_{\text{ext}} = 0$. As the σ can increase to 5 on Fig. 1), ecomes unstable must be a firstfurther heating σ_7 . However, on ecrease smoothly c the instability rst-order change ses smoothly on sis loop near the) in σ at T_5 on $t T_3$ on cooling; t on Fig. 1. The um width of this inically unstable 1 temperature T_4 + equals that at uilibrium would nd no hysteresis. g or 4' and 3' on to show that a letermining T_4 in

schematic sketch β^{T} in the critical ched from *below*, is to the value *B* s. On cooling, as nishes and jumps f the system is in $1/\beta^{T}$ never van-



ishes but has a singular point at T_4 . If the transition occurs in the metastable region but before the mechanical instability point is reached, $1/\beta^T$ will show hysteresis and discontinuities but does not vanish.

If an actual crystal behaves like this model, it is impossible to bring it arbitrarily close to a lambda point: a first-order transition occurs before the temperature reaches the theoretical critical temperature. Indeed, unless great care is taken to achieve true thermodynamic equilibrium, there are a range of temperatures (such as T_3 to T_5 in Fig. 1), where the properties depend on the history of the sample.

Constant Temperature

Let us look at the variation of area σ as a function of the applied pressure p_{ext} . Figure 2 shows, at a given temperature, the Ising pressure and the negative of the disordered-lattice pressure as functions of σ . At zero external pressure, the equilibrium point is at A, which corresponds to a largely disordered system. As the external pressure is increased, the ordering of the system increases and the area σ decreases smoothly until the pressure reaches a value equal to BB' at which mechanical instability occurs. The system spontaneously contracts to an area σ_C corresponding to Point C, which is the new equilibrium state under this external pressure of magnitude $p_3 = CC' = BB'$. A further increase in the external pressure causes a smooth decrease of the area and completes the ordering. If the pressure is now reduced, the system is mechanically stable until the area reaches the value $\sigma_D > \sigma_C$. At D the system is mechanically unstable and spontaneously expands to the value σ_E , the new equilibrium area under this pressure of magnitude $p_1 = EE' = DD'$. Again the possibility of hysteresis is predicted in a region which corresponds to metastable (or local) equilibrium. If



the system were in complete thermodynamic equilibrium a first-order transition without hysteresis would take place at pressure p_2 .

Constant Area

If the area is maintained constant by an applied pressure and not by rigid clamping, Inequality (10) is still valid. Therefore on each curve $p_I(T)$ for a given area, there is a forbidden zone in which the intersection of the isochores $-p_{dl}(T)$ and $p_I(T)$ does not correspond to a stable state. On Fig. 3 are plotted several Ising isochores corresponding to areas $\sigma_1 < \sigma_2 < \cdots \sigma_6 < \sigma_7$. The



FIG. 2. Behavior of a two-dimensional Ising model as a function of pressure at constant temperature. The insets represent schematically the pressure dependence of the area σ and of the reciprocal isothermal compressibility $1/\beta^{T}$.

1123