t aspects of the l. In this case, e Ising pressure if J and  $dJ/d\sigma$  simply related 609  $kT_c$ ) and it  $dJ/d\sigma < 0$ . Let ere n is a small pical disorderedar a small range

(11)

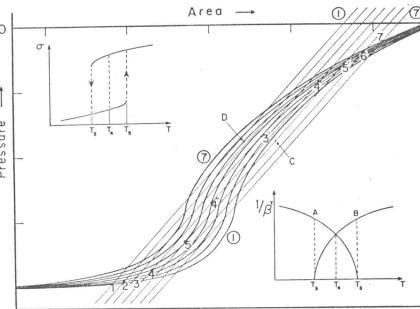
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ire

an external ap $p_{dl} + p_I$ . We nal pressure, for of  $p_I$  and  $-p_{dI}$  $T_2 < \cdots T_6 < T_7$ . e isotherms will xternal pressure fied (that is, if at of  $p_I$ ). Now  $p_{\rm ext} = 0$ . As the σ can increase to 5 on Fig. 1), ecomes unstable must be a firstfurther heating  $\sigma_7$ . However, on ecrease smoothly e the instability est-order change ses smoothly on sis loop near the in  $\sigma$  at  $T_5$  on t  $T_3$  on cooling; t on Fig. 1. The um width of this unically unstable temperature  $T_4$ 1 equals that at quilibrium would nd no hysteresis. g or 4' and 3' on to show that a letermining  $T_4$  in

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

Fig. 1. Behavior of a two-dimensional Ising model as a function of temperature at vanishing external pressure. The family of curves  $p_I$  were calculated at seven evenly-spaced temperatures from  $T_1$  to  $T_1$ . The family of straight lines— $p_{AI}$  were drawn to represent a disordered lattice with typical compressibility and thermal expansion coefficients. The encircled numbers 1 and 7 indicate the spin and lattice isotherms at  $T_1$  and  $T_2$ . The insets represent schematically the temperature dependences of the area  $\sigma$  and of the reciprocal isothermal compressibility  $1/\beta^T$ .



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  $\sigma$  as a function of the applied pressure  $p_{\text{ext}}$ . Figure 2 shows, at a given temperature, the Ising pressure and the negative of the disordered-lattice pressure as functions of  $\sigma$ . 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  $\sigma_C$  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  $\sigma_E$ , 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

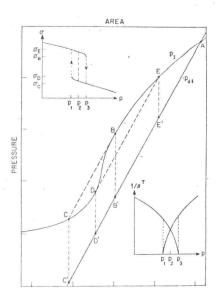


Fig. 2. Behavior of a two-dimensional Ising model as a function of pressure at constant temperature. The insets represent schematically the pressure dependence of the area  $\sigma$  and of the reciprocal isothermal compressibility  $1/\beta^T$ .