

where  $V$  is the volume and the subscript  $o$  refers to zero pressure. Quantities without an asterisk refer to the NaCl lattice, while quantities with an asterisk refer to the deformed lattice. For this deformation, the packing ratio,  $\beta$  is given by  $\beta = 2 - 6\eta^2 - 4\eta^3$ , and the next nearest neighbor distance,  $r_2 = r(3-6\eta)/(3+6\eta^2)$ , where  $\eta$  is the reaction coordinate or shear strain defined in Figure 1. We calculated the Gibbs free energy from

$$\frac{G^*}{K_o V_o} = \frac{F^*}{K_o V_o} + (P/K_o) \frac{V^*}{V_o} \quad (7)$$

at several reduced pressures for structures in the series NaCl  $\rightarrow$  CsCl. For the present calculation, we set the adjustable parameter  $n = 11$ . For each value of  $\eta$  and  $P/K_o$ ,  $V^*$  was adjusted to obtain the minimum value for  $G^*$ .

The results are plotted in Figure 2 in the form  $\Delta G/KV$ . The vertical displacement of each curve is arbitrary. Symmetry requires that the slope of the free energy curve be zero at  $\eta = 0$  and  $\eta = 0.2$ , while the curvature at  $\eta = 0$  is related to the

elastic constants in the NaCl lattice  $\left( \frac{1}{KV} \frac{\partial^2 \Delta G}{\partial \eta^2} = 6 \frac{C_{44}}{K} \right)$ . This

curvature is extrapolated by a dashed line in Figure 1, and the dashed line is a good approximation to the solid curve up to  $\eta \approx 0.1$ . A large part of the free energy difference between the two phases can be accounted for by this extrapolation. For  $P/K_o = 0$ ,  $C_{44}/K = 0.40$ , and there is a relatively large free energy difference. ( $C_{44}/K$  was calculated using equation (6) and equation A6 of Anderson and Demarest, 1971.) For  $P/K_o = 0.2$ ,  $C_{44}/K = 0.20$ , and the free energy difference is quite small. At about  $P/K_o = 0.3$  and  $C_{44}/K = 0.06$ , the free energies of the two phases are equal, and the phase transformation takes place.  $C_{44}$  does not vanish until a much higher pressure,  $P/K_o \approx 0.48$ .

Figure 2 shows that for this model,  $C_{44}/K \approx 0.06$  at the transition. We expect that changes in the interatomic forces from this simple model to real crystals will affect both  $C_{44}/K$  and  $\Delta G$  in a similar manner, preserving the result of a finite  $C_{44}/K$  at the transition.

There are at least two arguments which suggest that, for all transitions involving a finite displacement,  $C_t/K$  will not reach zero at the transition, where  $C_t$  is any shear constant.

1. There will always be a free energy barrier between the two stable phases at the transition. This corresponds to a hill on the curve of  $\Delta G$  versus  $\eta$  (Figure 2). (If there were a valley, this would correspond to a more stable phase.) Since the extrapolation of  $\Delta G$  based on  $C_t$  (the dashed line in Figure 1) will conform closely with the  $\Delta G$  curve, at least initially,  $C_t$  will be

positive. We expect that the size of the energy barrier and hence the value of  $C_t/K$  at the transition will be similar for similar compounds undergoing the same transition.

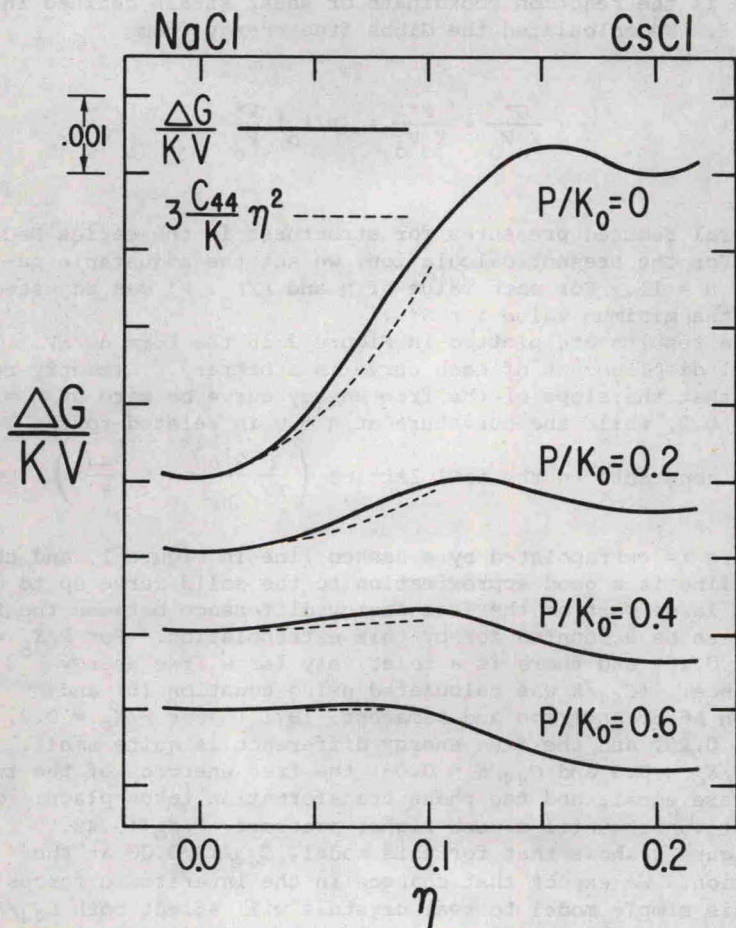


Fig. 2. Free energy change of a model crystal as it transforms from the NaCl to the CsCl structure.

2. If  $C_t = 0$  at the transition, there are three stable phases all having the same free energy (the two phases in question, and a shear distortion of the low-pressure phase). This is in violation of the Gibbs phase rule, since we are not including temperature in our analysis.