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, β 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 η is the reaction coordinate or shear strain defined in Figure 1. We calculated the Gibbs free energy from

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

at several reduced pressures for structures in the series NaCl → CsCl. For the present calculation, we set the adjustable parameter $n = 11$. For each value of η 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 ΔG 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 ΔG versus η (Figure 2). (If there were a valley, this would correspond to a more stable phase.) Since the extrapolation of ΔG based on C_t (the dashed line in Figure 1) will conform closely with the ΔG 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.
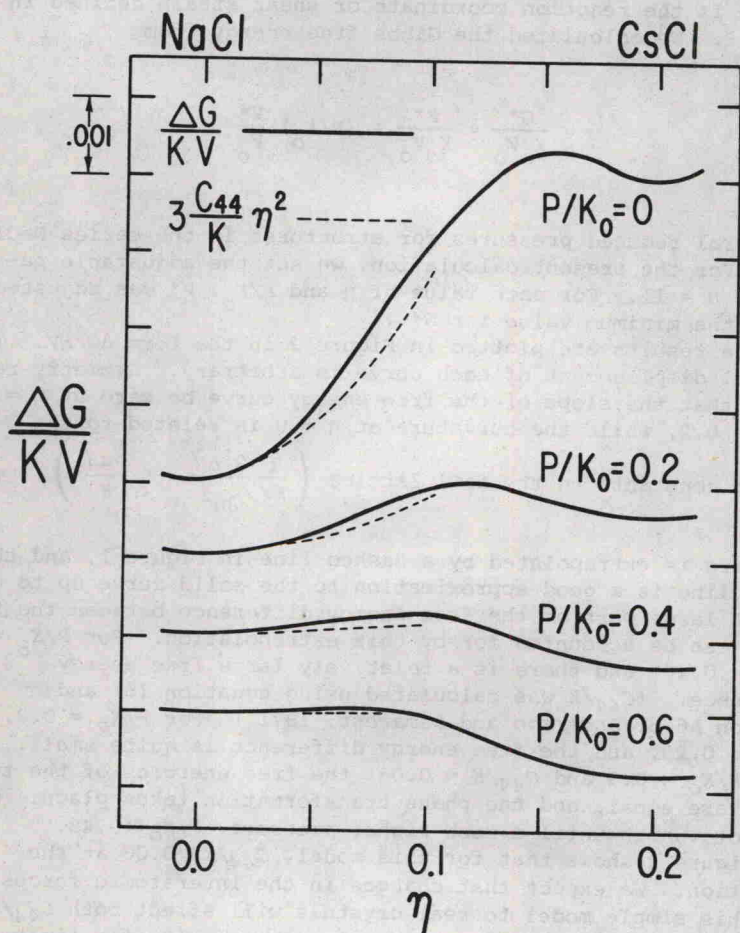

Fig. 2. *Free energy change of a model crystal as it transforms from the NaCl to the CsCl structure.*

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.