l. 28, pp. 350–351.

and the NaCl–CsCl
ation in RbI

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-3) that the spontaneous
rom the NaCl to the CsCl
re occurs via a structural
ishing of the frequency of
lattice vibrational mode at
zone face, at a pressure
rmation. This problem is
h extended by HARDY and
ndicate that, for appropri-
nteractions, as the solid is
transition conditions the
the lattice vibrational
shifted to lower energies
nes are shifted slightly to
n in Fig. 2 of HARDY and
f this note is to point out
are strongly inconsistent
es(4-6) of thermal expan-
rgy shifts calculated are
range to the transition.
uasi harmonic oscillator(7)
excitations are considered
early harmonic oscillators
ne dependence of their
This approximation leads
isen's Gamma":

$$= \frac{\sum_i \gamma_i C_{vi}}{\sum_i C_{vi}}$$

expansion coefficient, B_T
$/V$ is the heat capacity per

$$\frac{n\,\nu_i}{n\,V}$$

a", ν_i is any lattice vibra-
C_{vi} is the Einstein heat
de at the temperature of
tion is over all oscillators
vibrational spectrum. At
oscillator is classically

excited and its heat capacity equals the Boltzmann constant k, whence

$$\gamma_\infty = \frac{\sum_i \gamma_i}{3N}$$

the simple average of the mode gammas. At intermediate temperatures one sees that the mode gammas are weighted by their associated Einstein heat capacities at the observation temperature. Let us perform a qualitative analysis, estimating mode gammas from Fig. 2 of HARDY and KARO.

Compression data from Slater yields about 4 percent change in volume to the transition pressure. The average shift of the collected acoustic mode peaks is about 15 percent yielding an average acoustic mode gamma -4. Similarly, the average optical mode gamma is about $+0{\cdot}7$ yielding a high temperature limiting value of $\Gamma_G = -3{\cdot}3$ decreasing algebraically with decreasing temperatures. Since in equation (1) B_T, V and C_v must be positive, the implication of the negative gamma is that the thermal expansion coefficient have negative values at all temperatures. The thermal expansion coefficient of RbI has been measured over a wide temperature range.(4-6) Its value becomes negative at temperatures below 10°K but even at 5°K the value of γ estimated from the expansion data is about $-0{\cdot}2\times10^{-4}$, still less negative than value -4 suggested by the lattice dynamical calculations. (The low temperature limit of γ calculated from *measurements* of the pressure dependence of the elastic constants of RbI is positive.)

BARRON's suggestion(7) that the thermal expansion of solids is a quantity which yields information about the microscopic interactions in the solid is relevant here. In the present case, it seems that the requirement to account for the experimental values of the thermal expansion *and* to find a mode frequency which will vanish to permit spontaneous NaCl–CsCl transition will provide a challenge for the lattice dynamicists. We feel at present that the mode instability hypothesis probably is incorrect as the explanation of the spontaneous nature of the transformation on RbI.

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Note added by author in proof—Since submission of this paper, direct measurements have been reported by SAUDERSON, *Phys. Rev. Lett.* **17**, 530 (1966), using inelastic neutron scattering techniques at high pressure, of the shift of the Ta [100] mode energy with compression over the pressure range to the transformation. A decrease of only about 13 percent was observed, which is consistent with the suggestion of the present paper.

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