

much more under surface tension than do short, thick samples; it is possible that this contraction compensated the void formation. An attempt was made to polish some of our samples to look for voids, but the results were inconclusive; voids were certainly not present in such high concentrations on the cathode side as was the case with silver. Some voids were observed in GRONE's samples⁽¹⁰⁾ but were not convincingly distributed. Recent work by HERZIG⁽¹¹⁾ with stacks of copper foils indicated that impure copper shows a reversal whereas pure copper does not.

In conclusion, it appears that there is no intrinsic reversal in marker motion at high temperatures for pure copper. There was no tendency for the marker velocity to decrease in the hot regions, or even to slacken its exponential increase with temperature; the maximum temperatures of this experiment were well above those where previous reversals were observed. The reason for the reversal observed in previous work is still not clear.

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Lattice dynamics and the NaCl-CsCl transformation in RbI

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It has been suggested⁽¹⁻³⁾ that the spontaneous transformation of RbI from the NaCl to the CsCl structure at high pressure occurs via a structural instability caused by vanishing of the frequency of the transverse acoustic lattice vibrational mode at the center of the $\langle 100 \rangle$ zone face, at a pressure near that of the transformation. This problem is discussed and very much extended by HARDY and KARO.⁽³⁾ Their results indicate that, for appropriate choice of interionic interactions, as the solid is compressed toward the transition conditions the acoustic branches of the lattice vibrational spectrum are strongly shifted to lower energies while the optical branches are shifted slightly to higher energies as shown in Fig. 2 of HARDY and KARO.⁽³⁾ The purpose of this note is to point out that the results quoted are strongly inconsistent with the observed values⁽⁴⁻⁶⁾ of thermal expansion of RbI if the energy shifts calculated are linear over the pressure range to the transition.

Taking the familiar Quasi harmonic oscillator⁽⁷⁾ point of view the lattice excitations are considered to be those of a set of nearly harmonic oscillators which exhibit a volume dependence of their characteristic energies. This approximation leads to the result for "Grüneisen's Gamma":

$$\gamma_G \equiv \frac{\alpha B_T V}{C_v} = \frac{\sum_i \gamma_i C_{vi}}{\sum_i C_{vi}}$$

in which α is the thermal expansion coefficient, B_T is the Bulk Modulus C_v/V is the heat capacity per unit volume,

$$\gamma_i \equiv \frac{d \ln \nu_i}{d \ln V}$$

a so called "mode gamma", ν_i is any lattice vibrational frequency and C_{vi} is the Einstein heat capacity of the i 'th mode at the temperature of observation. The summation is over all oscillators making up the crystal vibrational spectrum. At high temperature each 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 $+0.7$ yielding a high temperature limiting value of $\Gamma_G = -3.3$ 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 -0.2×10^{-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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... Eisen's Gamma":

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

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

... $\frac{\sum_i \gamma_i C_{vi}}{\sum_i C_{vi}}$
... γ_i is any lattice vibra-
... C_{vi} is the Einstein heat
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