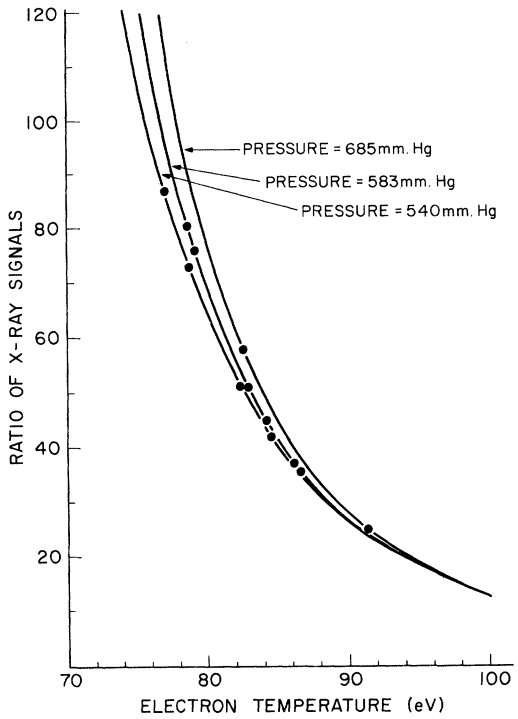

FIG. 3. Electron-temperature measurements of laser sparks in neon at pressures of 540, 583, and 685 mm of mercury.

This is supported by the fact that the temperatures observed can be correlated, on the basis of the detonation model,[3,4] with the velocity of the luminous front obtained from streak photographs.

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PRESSURE DEPENDENCE OF THE TA[100] ZONE-BOUNDARY PHONON FREQUENCY IN RUBIDIUM IODIDE

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The frequency of the TA[100] zone-boundary phonon has been measured in rubidium iodide under hydrostatic pressures of 0 to 3.72 kbar by neutron inelastic scattering. A linear fit to the percentage decrease in frequency gives a value of 13.5 ± 0.9 % when extrapolated to the NaCl-CsCl polymorphic transition pressure.

Under a uniform hydrostatic pressure of 3.97 kbar,[1] rubidium iodide undergoes a polymorphic transition from a fcc structure (NaCl type) to a bcc structure (CsCl type). By measuring the pressure dependence of the elastic constants, Daniels and Smith[2] disposed of an earlier suggestion that the transition resulted from instability of the NaCl phase to finite strain along a ⟨111⟩ direction, and suggested instead that the lattice becomes unstable to short-wavelength shear motion. In terms of the phonon description of lattice dynamics, they postulated that the frequency of the transverse acoustic phonon at the [100] zone boundary becomes zero at the transition point, and that the lattice therefore becomes physically unstable to this mode.

Hardy and Karo,[3] following this suggestion, showed that such an instability could be predicted by a plausible model of the interionic forces fitted to measured or estimated values of elastic constants, restrahlung frequency, and the lattice parameter at the transition point. In order to achieve instability, their model required the inclusion of contributions from a short-range, three-body type of interaction.[4]

The object of the experiment reported in this Letter was the direct measurement by a neutron-inelastic-scattering method of the frequency of this particular phonon as a function of pressure. Extensive measurements of phonon frequencies in a number of symmetry directions of rubidium iodide at atmospheric pressure have been made on the DIDO triple-axis spectrometer.[5] These confirm the general features of the dispersion relations calculated by Hardy and Karo using the same model but fitted to standard temperature and pressure parameters.[6] In particular, the measurements confirm the low frequencies of the TA[ξ00] branch, although the observed values were about 10% higher than the calculated values.

The pressure measurements were made on a 2-in.-long, 1-in.-diam cylindrical single crystal immersed in a small quantity of hydraulic oil in a thin-walled steel vessel designed to operate at pressures up to 3.8 kbar. The low frequency of the phonon resulted in a high cross section for the scattering process which partly offset the 80% loss of intensity due to the pressure vessel walls. The shielding required to minimize background scattering, and contain fragments of a bursting vessel, restricted the region of the reciprocal lattice that could be observed by the spectrometer. Within this region there was sufficient flexibility to allow measurements of scattered neutron spectra over energy transfers corresponding to a phonon frequency range of 0 to 1.2 THz (10^{12} cps), while maintaining the momentum transfer fixed with respect to the lattice (constant $\vec{Q}$ mode of operation).

The results obtained at eight values of the pressure are shown in Table I. The momentum transfer for all the measurements corresponds to the point (610) in the reciprocal lattice, the orientation of this vector with respect to the [010] direction ensuring that only modes of transverse polarization could be excited. Corrections have been made to the raw data, firstly for all scattering other than coherent processes in the crystal, and secondly for a sharp peak centered at zero energy transfer arising from second-order contamination of the incident and scattered neutron beams being Bragg reflected by the (1220) planes in the sample.

Table I. Observed TA[100] Phonon Frequencies.

Pressure (kbar)	Frequency [THz(10^{12} cps)]	Observed peak rms deviation (THz)
0	0.676 ± 0.020	0.142
0.69	0.652 ± 0.025	0.142
2.07	0.640 ± 0.025	0.162
2.62	0.638 ± 0.020	0.172
2.76	0.623 ± 0.025	0.148
3.17	0.591 ± 0.020	0.176
3.45	0.592 ± 0.020	0.190
3.72	0.583 ± 0.020	0.180

Figure 1 shows the frequency shift, expressed as a percentage of the frequency at atmospheric pressure, ν_0, plotted against pressure. The errors shown in the figure arise partly from counting statistics and partly from uncertainty in the method of removing the second-order Bragg background from the low-frequency wing of the phonon peak. Certain systematic errors affecting the accuracy of the absolute frequencies (Table I) cancel out in the relative values of frequency shift. Because of an uncertainty of about 0.15 kbar in the mea-

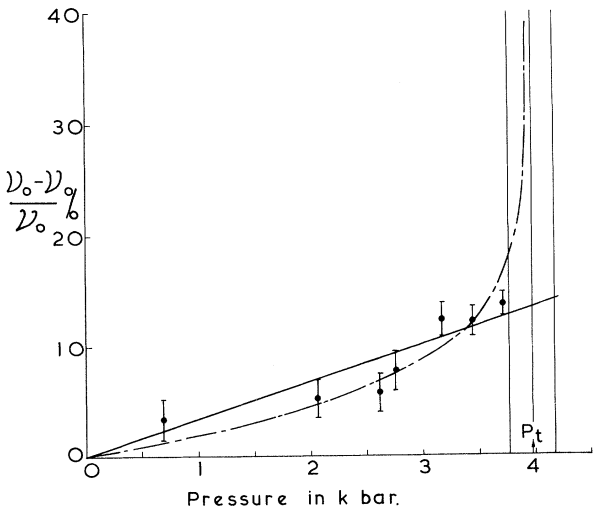

FIG. 1. Relative frequency shift versus pressure. Full line $(\nu_0-\nu)/\nu_0 = 0.0345P$; broken line, $\nu/\nu_0 = (1-P/P_t)^{0.065}$; shaded zone, minimum hysteresis.[7]

surement of the pressure on the sample during the experiment, a closer approach of the transition pressure than $0.94P_t$ was avoided as a partial or complete transition would have resulted in the destruction of the single crystal. A weighted, least-squares fit to a simple linear relation is shown in the figure. It has a slope of $(3.45 \pm 0.22)\%$/kbar which, when extrapolated, gives a value for the shift at the transition pressure of $(13.5 \pm 0.9)\%$. This is clearly far short of the 100% required for instability. The effects of finite resolution have been considered, but using values of the curvature of the dispersion surfaces derived from the Hardy and Karo calculations and the known shape and orientation of the momentum resolution functions, which were deliberately arranged to minimize these effects, an upward correction of no more than one or two percent is obtained.

The dimensionless parameter $\gamma_i = -d(\ln\nu_i)/d(\ln V)$, where V is the volume of the unit cell, is related to the Grüneisen parameter and expresses the effect of a dilation of the lattice on the frequency of a given mode. The value of $\gamma_{TA[100]}$ deduced from the linear fit to the neutron data is -3.32, compared with -1.15 for $\gamma_{TA[\xi 00]}$ measured by Daniels and Smith in the nondispersive, velocity-of-sound region of very small ξ. Negative values are abnormal and imply a decrease in stiffness of the lattice to the particular mode under compressive strain. Such behavior would appear probable in a low-pressure phase approaching a normal first-order transition. The condition for such a transition is simply that as the pressure increases through P_t, the minimum in the Gibbs free energy corresponding to the CsCl configuration falls below the minimum corresponding to the NaCl configuration. The "mode instability" theory imposes the much more stringent condition that at P_t the NaCl phase no longer corresponds to a minimum, i.e., it is not even metastable.

It might be argued that the data, which end at $0.94P_t$, could still be fitted by a nonlinear relation going to 100% at P_t. To obtain some measure of the nonlinearity required, a power-law relation of the form $\nu/\nu_0 = (1-P/P_t)^n$ has been fitted to the data. It is found that the value of the exponent must lie in the range $0.05 < n < 0.09$. The curve for $n = 0.065$ is shown in Fig. 1. Within the accuracy of the measurements this fit is acceptable, but a sharp functional behavior of this type is inconsistent with the large degree of hysteresis exhibited by the transition. Typical values of ± 1 kbar are observed[7]; the minimum observed values (± 0.2 kbar), which were obtained by Bridgman in nonideal conditions,[8] are shown in Fig. 1.

Although the statistical accuracy of the data is too low for detailed analysis of line shapes, the rms deviations of the observed peaks are listed in Table I. These show a definite trend towards increased width as the transition pressure is approached. Since the spectrometer resolution remains constant, this indicates an increase in the intrinsic linewidths resulting from anharmonicity. No attempt has been made to extract numerical values for the intrinsic linewidths because an apparent over correction for background in the wings of the peaks gives total widths that are smaller than the resolution, but allowing for this, the maximum intrinsic width is about 15 to 20% of the mean frequency. At present, there is no theory describing the anharmonic behavior of a lattice at a first-order polymorphic transition with which the neutron data can be compared.

It is concluded that the hypothesis that the NaCl-CsCl phase transition in rubidium iodide is due to the onset of instability to the TA[100] normal mode is not supported by the neutron data, nor is there evidence of appreciable anharmonicity appearing within 6% of the transition pressure. However, the low frequency of these shear modes does suggest that the activation energy require to pass to the eightfold bcc coordination is small, and this is constant with Bridgman's observations of the temperature independence of P_t above 300°K.[8]

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LOCALIZED VIBRATIONS OF TRAPPED MOLECULES

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The spectrum of motions of molecules trapped in molecular cages has been studied in detail by neutron inelastic- and elastic-scattering methods. These experiments are related to those on the vibration of hydrogen atoms and ions in crystal lattices. Typical of these is the almost Einstein-like vibration of the hydride ion in zirconium hydride which was studied originally by Pelah et al.[1] More recently the first, second, and third vibrational modes of hydrogen in the related nonstoichiometric titanium hydride, $TiH_{1.6}$, have been observed by Pan and Webb.[2] In such experiments the high neutron-proton scattering cross section causes the hydrogen scattering to dominate over that for other atoms. In extending this type of measurement to hydrogeneous molecules trapped in molecular cages, the interesting extra dimension of the intramolecular modes enters the problem. In suitable cases these should show up in the neutron-scattering spectrum as well as the motion of the whole molecule in the cage. The interaction between these modes and the lattice vibrations is of considerable interest, and evidence for this in several systems with different types of guest-host potential is reported here.

We have carried out experiments on methane, methyl cyanide, and methanol trapped in β-quinol[3] clathrates, and on methyl cyanide, methanol, water, and ammonia in molecular sieves.[4] Two forms of quinol were used: a fully deuterated form $C_6D_4(OD)_2$ abbreviated to (QD_6) and another form in which the protons of the OH groups only, were replaced by deuterium [$C_6H_4(OD)_2$]. The results in the fully deuterated lattice only will be discussed in detail here. Replacement of each hydrogen in the lattice by deuterium lowers the total scattering cross section from 80 to about 7 b, and is a suitable procedure in general for minimizing the scattering of host lattices containing hydrogen. The apparatus used has been described by Harris et al.,[5] and provides a monokinetic beam of 5.3-Å neutrons from a liquid-hydrogen moderator. This beam is scattered from the sample under investigation, and the spectrum of scattered neutrons is recorded at angles between 20° and 90° to the incident beam.

A selection of results is presented in Figs. 1-3. In each case the spectrum of the scattered neutrons may be divided into an elastic and an inelastic region. The elastic peaks are at longer times of flight, as the neutrons, scattered inelastically from the room-temperature

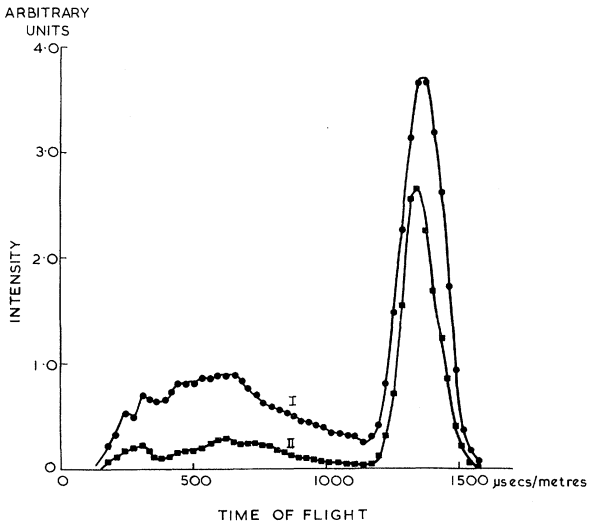

FIG. 1. Neutron time-of-flight spectrum of the motions of CH_3OH in fully deuterated β quinol at 300°K for neutrons scattered through 90°. (I) Spectrum of lattice + molecule. (II) Spectrum of lattice alone.