material was Ohmic up to 10^4 V/cm where the electron velocity was 7×10^6 cm/sec, setting this value as a lower limit for the saturation velocity. It is conceivable that in Zn-doped GaN this limit could be lower.

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Measurement of Selected Phonons in Rubidium as a Function of Temperature and Volume*

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The first measurements of phonon frequencies in a metal as a function of temperature, at constant values of the atomic volume, are reported. The [ζ00]T, $\zeta=0.2$ mode exhibits considerable temperature dependence at constant volume, whereas modes in the [ζ00]L, [ζζ0]L, and [ζζ0]T1 branches show little such dependence. The mode Grüneisen parameters are also determined.

In this Letter we report the first neutron-scattering measurements of normal modes of vibration in a metal, as a function of temperature from 80 to 295 K, for fixed values of the volume between (79 and 89)$\times10^{-24}$ cm^3 atom^{-1}. The temperature dependence of the phonon spectrum at atmospheric pressure has been studied in many materials, including Rb,[1] and the pressure dependence of selected normal modes, at room temperature, has been measured in a few crystals, including RbI,[2] Pb,[3] NaI,[4] and Na.[5] In addition, experiments to determine anharmonic effects at constant volume in Ne[6] and He[7] have been reported. Rubidium was selected for the present study because the harmonic dynamical properties are reasonably well understood, and there exists a volume-dependent effective potential[8] which has been successfully used to compute a number of properties in both the solid[9,10] and liquid[11] states. Furthermore the metal has a large compressibility[12] and thermal expansivity,[13] as well as favorable neutron cross sections.

The sample, a single crystal of Rb 5.2 cm long and 1.6 cm in diameter with a [001] direction close to the cylindrical axis, was grown by a modified Bridgman method.[14] The crystal was contained in a 7075-T6 aluminum pressure vessel with a minimum outer diameter of 6.4 cm, which was designed and lent to us by Professor W. B. Daniels of the University of Delaware. The vessel was housed in a variable-temperature liquid-nitrogen cryostat, and hydrostatic pressure was applied using a two-stage helium-gas-generating system,[15] on loan from Argonne National Laboratory. The measurements were made using the HB-4A triple-axis spectrometer at the high-flux isotope reactor, Oak Ridge National Laboratory. We used a fixed incident energy of 13.6 meV (3.30 THz), produced by Bragg reflection from a pyrolytic graphite (002) monochromator; a pyrolytic graphite filter was employed to remove higher orders, and a zinc (002) crystal was used as analyzer. The measurements were made using the constant-$\vec{Q}$ mode of operation.

Data were obtained at four temperatures. At each temperature T the pressure P was adjusted to obtain selected values of the lattice parameter a (Table I). In each case a was determined by measuring the scattering angles for various Bragg reflections. By extrapolating our 295-K data to 5 kbar, we obtain $a=5.408$ Å giving a ratio of 0.854 for the atomic volumes at 0 and 5

TABLE I. Measured values of the lattice parameter a for various temperatures T and pressures P. The estimated errors for a and P are better than ±0.005 Å and ±0.01 kbar, respectively. The values of a for $P=0$ were obtained by interpolation of the numbers given in Ref. 10.

$T=80$ K		$T=150$ K		$T=230$ K		$T=295$ K	
P (kbar)	a (Å)	P (kbar)	a (Å)	P (kbar)	a (Å)	P (kbar)	a (Å)
0	5.610	0	5.637	0	5.670	0	5.700
1.86	5.502	0.28	5.622	0.71	5.620	0.34	5.675
2.36	5.475	2.26	5.502	2.71	5.502	1.02	5.620
4.23	5.394	4.43	5.402	4.61	5.408	2.07	5.555
						3.02	5.502
						3.75	5.470
						4.75	5.420

kbar, whereas Vaidya, Getting, and Kennedy[12] obtained a value of 0.862 for this quantity. Our data at 80 K are insufficient for us to make a useful comparison with the work of Gutman and Trivisonno.[16]

In Fig. 1 we show some neutron groups for the best-determined mode, $[\zeta 00]$T at $\zeta=0.2$. Clearly the frequency of this mode changes both with V at constant T and with T at constant V. There is also evidence of an increase in the width of this mode with increasing T. Figure 2 shows a selection of our results for the frequencies of four normal modes. Since the results for $a=5.41$ Å were in fact obtained for slightly different values of a (see Table I), small corrections (<0.01 THz) were applied to these data, using mode Grüneisen parameters determined from this experiment (see below). Note that our results have not been corrected for instrumental resolution: Only the $[\zeta\zeta 0]$T1 mode would be significantly affected.[1]

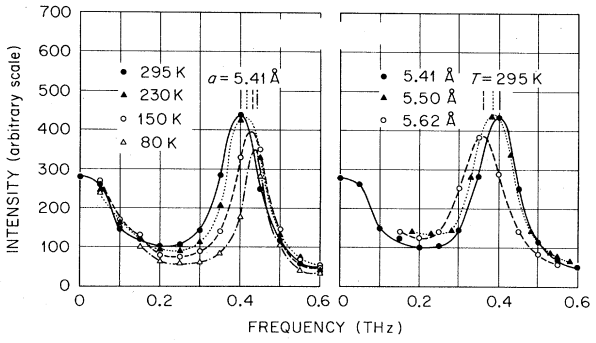

FIG. 1. Neutron groups for the $[\zeta 00]$T, $\zeta=0.2$ mode, measured at $\vec{Q}=[2, 0.2, 0]\times 2\pi/a$, normalized to the same number of monitor counts. The lines are drawn to guide the eye.

From Fig. 2 it is clear that only one mode, $[\zeta 00]$T at $\zeta=0.2$, shows a definite change in phonon frequency with temperature, at constant volume. Using our data at the four temperatures we have computed average values for the zero-pressure mode Grüneisen parameters $\gamma_i \equiv -\partial \ln \nu_i / \partial \ln V$, as follows: $[\zeta 00]$L, $\zeta=0.2$, 2.15 ± 0.23; $[\zeta\zeta 0]$L, $\zeta=0.2$, 1.65 ± 0.07; $[\zeta 00]$T, $\zeta=0.2$, 0.99 ± 0.13; and $[\zeta\zeta 0]$T1, $\zeta=0.3$, 1.31 ± 0.25. Copley[10] computed Grüneisen parameters of 2.1, 1.7, 1.1, and 3.4, respectively. The calculated parameter for

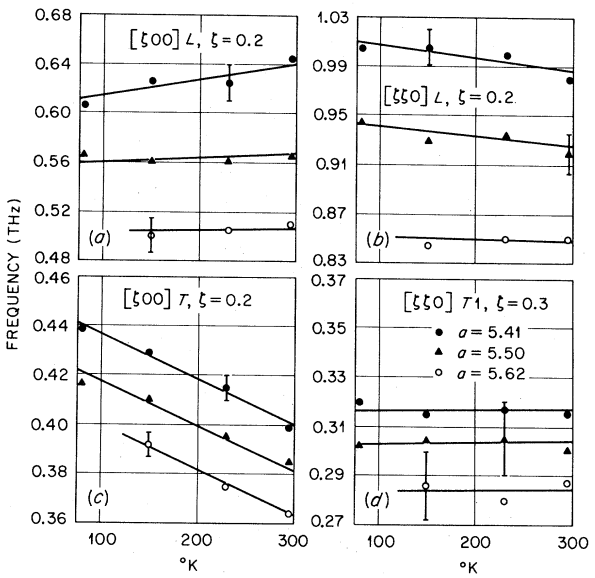

FIG. 2. The temperature dependence of four normal modes, for three values of the lattice parameter. Typical error bars are shown. Note the different ordinate scales. The modes shown in (a), (b), (c), and (d) were measured at $\vec{Q}$'s of $\{[2.2, 0, 0], [1.2, 1.2, 0], [2, 0.2, 0],$ and $[0.7, 1.3, 0]\}\times 2\pi/a$, respectively. The lines are drawn to guide the eye.

the $[\zeta\zeta 0]$T1 mode is clearly far too large, but for the other modes the agreement between calculation and experiment is very encouraging.

Since the $[\zeta 00]$T, $\zeta = 0.2$ mode shows definite dependence on T at constant V (Fig. 2), it is clear that the quasiharmonic approximation is insufficient. It should be remembered that, to first order in anharmonic perturbation theory, *two* contributions to the phonon self-energy must be included. Calculations[10,17] have shown that for most branches the two contributions are of opposite sign and largely cancel. Thus the absence of a detectable shift in a mode's frequency, with T at constant V, does not imply the absence of anharmonicity. Though we cannot explain the fact that only the $[\zeta 00]$T mode shows an appreciable shift, we would offer two comments. First, the constant-volume anharmonic shifts in neon,[6] for the $[\zeta 00]$ branches at small ζ, show a similar behavior to that observed in Rb. Second, the present results are consistent with the fact that the calculated[10,17] cubic and quartic shifts in Rb and K, for the $[\zeta 00]$T branch, are of the same sign (negative with increasing T), whereas the corresponding shifts for the $[\zeta 00]$L, $[\zeta\zeta 0]$L, and $[\zeta\zeta 0]$T1 branches are of opposite sign. However, it is not clear why this particular result follows from the anharmonic calculations.

This investigation represents the first attempt at a detailed study of the lattice dynamics of a metal as a function of both temperature and volume. Considerable experimental difficulties exist because of inevitable scattering from the pressure vessel and demands on instrumental resolution. Nevertheless the measurements clearly provide valuable data for comparison with anharmonic calculations. Further measurements are planned for the near future.

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