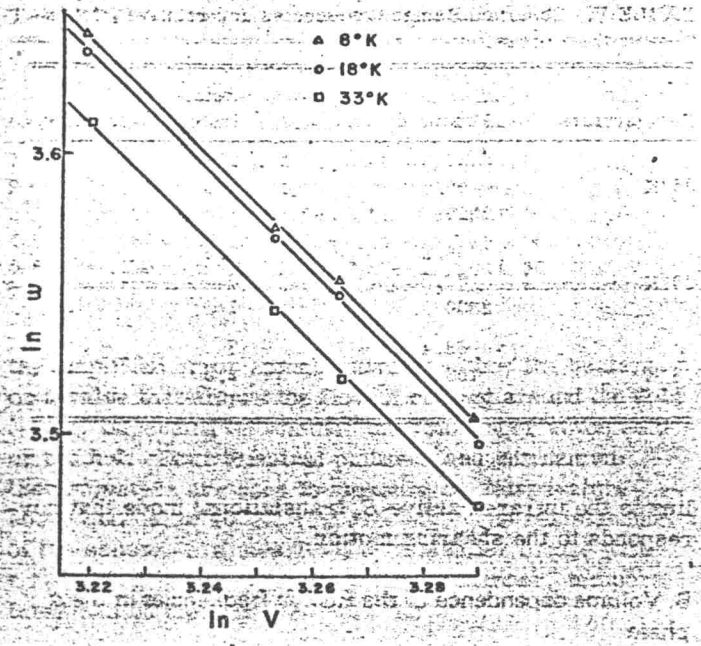

FIG. 5. Plot of $\ln\omega$ versus $\ln V$ for the E_g mode of the α phase, where the frequency ω is in cm^{-1} and the molar volume V is in cm^3/mole: ×, experimental points; ——, best fit to a straight line.

potential, especially the short-range repulsive part.

The Grüneisen parameters for the librational modes were obtained using the data in Table VI. In Figs. 5–7, constructed from this data, $\ln\omega$ is plotted versus $\ln V$ for each of the modes. Also shown in Fig. 5 are data points for the E_g mode from sample 6. The data points were fitted to a straight line, shown by solid lines in the figures. The negative slope of each line is the Grüneisen parameter for that particular mode. The Grüneisen

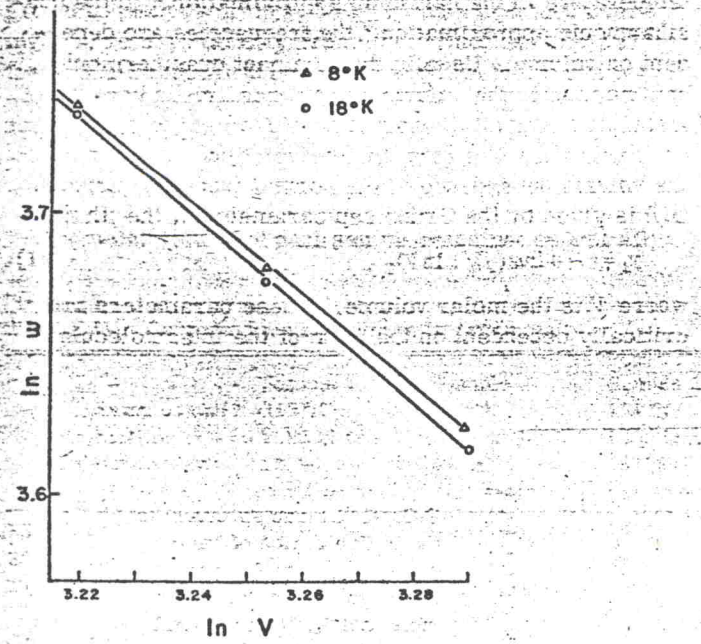

FIG. 6. Plot of $\ln\omega$ versus $\ln V$ for the low-frequency T_g mode of the α phase, where the frequency ω is in cm^{-1} and the molar volume V is in cm^3/mole: ×, experimental points; ——, best fit to a straight line.

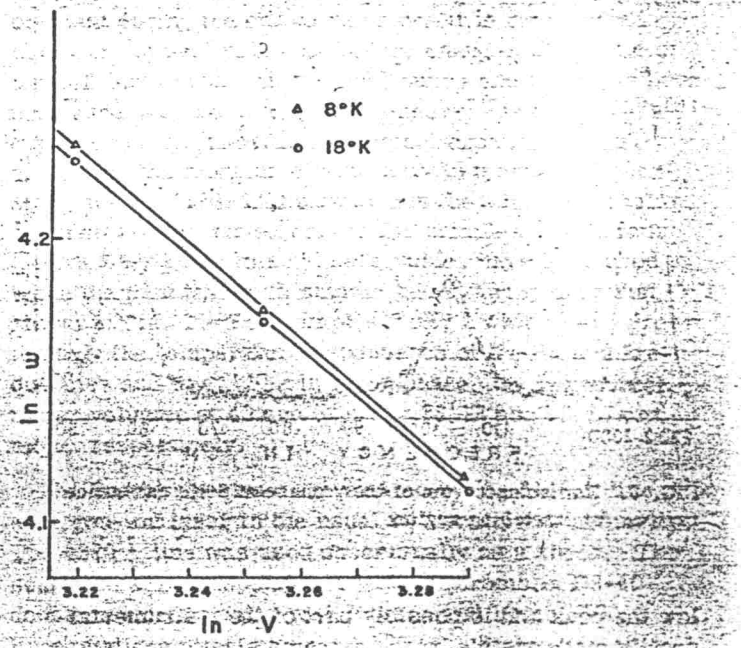

FIG. 7. Plot of $\ln\omega$ versus $\ln V$ for the high-frequency T_g mode of the α phase, where the frequency ω is in cm^{-1} and the molar volume V is in cm^3/mole: ×, experimental points; ——, best fit to a straight line.

parameters and estimated errors were determined using a least square fit. The results are summarized in Table VII. The measured Grüneisen parameters are independent of temperature within the experimental errors. They are substantially higher than the result of $\frac{5}{6}$ expected for a quadrupolar interaction potential in the quasiharmonic approximation. This result of $\frac{5}{6}$ follows from the relation $\omega^2 \propto r^{-5}$ between the librational frequency ω and the intermolecular distance r. The spectroscopic values are closer to the value $1.0 \leq \gamma \leq 1.5$ obtained by Brookeman, McEnman, and Scott[39] using nuclear quadrupole resonance methods.

Zunger and Huler[36] used a 6–12 atom–atom potential and obtained Grüneisen parameters around 3 for the librational modes of the α phase. Raich, Gillis, and Anderson[49] used this potential in a self-consistent calculation and obtained Grüneisen parameters 15%–50%

TABLE VI. Volume dependence of the Raman spectrum in the α-phase.

T (°K)	Frequency (full width at half-intensity) (cm^{-1}) E_g	T_g	T_g	Relative peak intensities $E_g : T_g : T_g$	Molar volume (cm^3/mole)
8	33.3[a]	37.5[a]	61.3(4.5)	3.6:1:0.05	26.82
	35.6(0.8)	39.7(0.8)	65.0(5)	3.6:1:0.05	25.87
	38.2(0.8)	42.0(0.8)	69.0(5)	4.2:1:<0.05	25.00
18	33.0(1.7)	37.2(1.7)	61.0(5.5)	4.7:1:0.05	26.83
	35.5(1.7)	39.5(1.7)	64.8(6)	5.2:1:<0.05	25.87
	38.0(1.7)	41.9(1.7)	68.6(6)	5.5:1:<0.05	25.01
33	32.3(8)	...	...	...	26.84
	34.6(8)	...	...	...	25.88
	37.0(8)	...	...	...	25.02

[a]These lines are very narrow and the linewidths cannot be resolved from the instrumental widths.