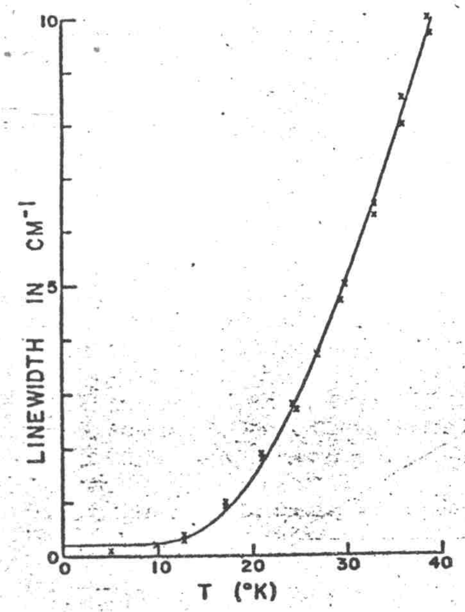

FIG. 9. Temperature dependence of the true linewidth of the E_g line of the α phase: $\times$, experimental points obtained assuming that both the true line and the instrumental profile are given by Lorentzian curves; ——, best fit to the function in Eq. (9).

where $\omega_1 = \frac{1}{2}\omega_0(\lambda)$ and $\omega_2 = \frac{1}{3}\omega_0(\lambda)$, and $\Gamma_1(\lambda)$ and $\Gamma_2(\lambda)$ are temperature independent.

The linewidths from Table VIII were fitted to the function given in (8), but both sets of values resulted in extremely poor fits. The difficulty arising in these fits seems to be the smallness of the linewidth at very low temperatures. This is easily resolved by considering the second term in (7). This term will go to zero at 0 °K. Then, the small linewidth observed at 5 °K can be attributed to other less important anharmonic interactions.

If there is one dominant cubic anharmonic interaction that allows the E_g libron to combine with a second excitation to produce a third, Eq. (7) becomes

$$\Gamma(\lambda) = \Gamma_1(\lambda) + \Gamma_2(\lambda)\left[n(\omega') - n(\omega + \omega')\right] \tag{9}$$

where ω, ω', and $\omega'' = \omega + \omega'$, refer to the frequencies of

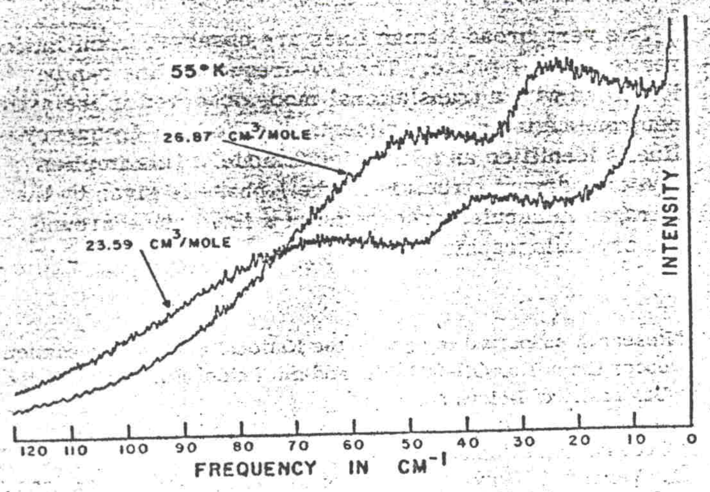

FIG. 10. Raman spectra in the β phase at 55 °K from samples with molar volumes of 23.59 and 26.87 cm³/mole. Instrumental resolution is 2 cm⁻¹.

TABLE IX. Volume dependence of Raman frequencies in the β phase at 55 °K.

Sample	Molar volume (cm³/mole)	Frequencies (cm⁻¹)	
1	26.87	25 ± 3	50 ± 3
2	25.90	28 ± 3	54 ± 3
3	25.05	31 ± 3	58 ± 3
4	23.59	36 ± 3	68 ± 3

the E_g libron and the other two excitations, respectively. The term $\Gamma_1(\lambda)$ has been added to account for the small linewidth near 0 °K.

The two sets of linewidths were fitted to the function given in equation (9) with $\omega = 35$ cm⁻¹. Figure 9 shows the best fit for the set of linewidths not in parentheses in Table VIII. The resulting parameters are $\Gamma_1(\lambda) = 0.2$ cm⁻¹, $\Gamma_2(\lambda) = 140$ cm⁻¹, $\omega' = 63$ cm⁻¹, $\omega'' = 98$ cm⁻¹; and $\Gamma_1(\lambda) = 0.6$ cm⁻¹, $\Gamma_2(\lambda) = 106$ cm⁻¹, $\omega' = 54$ cm⁻¹, $\omega'' = 89$ cm⁻¹. The errors in these results are probably large and difficult to estimate. However, they show that the process responsible for the temperature dependence of the linewidth of the E_g line is possibly a combination with a T_g libron to create a T_u phonon. The reverse process of a T_u phonon decaying into E_g and T_g librons has been proposed as an explanation for the anomalous width of the infrared-active T_u phonon with a zero pressure frequency of 70 cm⁻¹.[46] Although the characteristic frequencies ω' and ω'' are larger than those corresponding to the low-frequency T_g libron and the infrared-active T_u phonon in samples 5 and 6, the discrepancies might be due to the failure to consider other less important anharmonic processes.

The coefficient $\Gamma_2(\lambda)$ can be related to the cubic anharmonic term H_3 in the Hamiltonian. Using $\Gamma_2(\lambda) = 120$ cm⁻¹ results in $|H_3|^2 \simeq 1.2(\text{cm}^{-1})^2$ in good agreement with the value of about $1(\text{cm}^{-1})^2$ estimated by Harris and Coll[46] for the cubic anharmonic interaction which allows the infrared-active T_u phonon to decay into two librons.

E. β phase

Figure 10 shows Raman spectra in the lattice region of the β phase for samples one and four at 55 °K. Two extremely broad lines are seen, whereas previous workers observed only a wing on the Rayleigh line.[20] Indeed, the high-frequency tail of the spectrum resembles the wing of the Rayleigh line in the fluid phase. In the stretching region, not shown in the figure, a single line is observed having a wing on each side. Table IX summarizes the results for samples one to four at 55 °K. These frequencies are obtained by fitting Gaussian curves after subtracting a background having the shape of the Rayleigh wing in the fluid and drawn to fit the high-frequency tail of the spectrum in the β phase. Table X shows the temperature dependence of the Raman frequencies for sample four.

Figure 11 shows a plot of lnω versus ln$V$ for the two Raman lines of the β phase at 55 °K. The straight lines that fits the data best are shown by solid lines and result in Grüneisen parameters of 2.8 ± 0.5 and 2.4 ± 0.5 for the low- and high-frequency lines.