TABLE VII. Grüneisen parameters for the librational modes in the α phase.

T (°K)	E_g mode	Low-frequency T_g mode	High-frequency T_g mode
8	1.95±0.06	1.63±0.06	1.68±0.08
18	1.95±0.06	1.68±0.06	1.65±0.08
33	1.96±0.08		

larger than the measured values. These results seem to indicate that the 12 power of the repulsive part is too high. Indeed, for a repulsive atom–atom potential of the form Ar^{-n}, the Grüneisen parameters obtained in the present study would yield $9.3<n<10.1$ and $7.4<n<8.4$ for the E_g and T_g modes, respectively, in the quasi-harmonic approximation. This conclusion is substantiated by the classical harmonic calculations of Jacobi and Schnepp,[47] who used the 6–n atom–atom potential and found $n=9$ to give better agreement with the measured lattice energy, and infrared and Raman frequencies at zero pressure. Using a multipole expansion of the intermolecular potential Mandell[50] obtained Grüneisen parameters of about 2 and 1.7 for the E_g and two T_g modes, respectively. However, the author's assumption of a hexadecapole–monopole term independent of volume is not fully justified.[50]

The measured librational frequencies can be extrapolated to zero pressure using the Grüneisen parameters and the molar volumes at zero pressure from Fig. 1. The calculated zero pressure librational frequencies are 32.8, 37.0, and 60.5 cm^{-1} at 8 °K and 32.3, 36.6, and 60.1 cm^{-1} at 18 °K to be compared to 31.5, 36.0, and 59.8 cm^{-1} measured by Mathai and Allin[22] at 4 °K and 32, 36.5, and 60 cm^{-1} measured by Anderson, Sun, and Donkersloot[21] at 18 °K.

The band between 70 and 100 cm^{-1} in Fig. 4 seems to consist of a series of broad lines, the most pronounced being around 70 and 95 cm^{-1}. These frequencies are close to the sum of the E_g and each of the T_g librational modes, indicating that it might be a two-libron band. However, the 70 cm^{-1} line could coincide with an infrared-active phonon.[24–26] To check these possibilities, the Grüneisen parameters of both lines at 8 °K were estimated to be 2.2 and 2.0, respectively. These values are close to those obtained for the librational modes and favors its identification as a two-libron band, as previously suggested.[46]

The individual Grüneisen parameters are related to the Grüneisen gamma γ_G and other thermodynamic functions by

$$\frac{1}{C_V}\sum_j \gamma(j)C_{Vj}=\gamma_G=\frac{\alpha V}{C_V K_T}\,, \tag{2}$$

where C_{Vj} and C_V are the heat capacity at constant volume for the jth mode and the solid, respectively; α is the volume coefficient of thermal expansion; and K_T is the isothermal compressibility. Heberlein, Adams, and Scott[15] calculated γ_G using experimental values of the other thermodynamic functions in Eq. (2). They obtained a γ_g strongly temperature dependent above 16 °K, leveling off to a value around 3 just below the α–β transition. Since the Grüneisen parameters for the librational modes are substantially lower than three, it must be concluded that these modes cannot be responsible alone for the increase in γ_G. Translational modes probably having Grüneisen parameters around 3 must make significant contributions to γ_g below 36 °K.

C. Temperature dependence of E_g librational frequency in the α phase

In an isobaric experiment, the changes in the librational frequencies with temperature contain one contribution due to thermal expansion and a second contribution which is a direct result of anharmonic interactions and is present even in a solid held at constant volume. This last contribution has been measured in samples five and six. The change in molar volume of these "clamped" samples in the temperature range 5–39 °K introduces a change in the E_g librational frequency of about 0.05 cm^{-1}. This change is considerably less than the errors in the frequencies and it is reasonable to assume that the Raman spectrum in the α phase for these samples is only directly affected by changes in temperature. The E_g librational frequencies of these samples are given in Table VIII at intervals of about 3 °K in the temperature range 5–39 °K.

Although the librational amplitudes are large in the α phase, Harris and Coll[46] have shown that they are small enough to warrant a perturbation treatment starting from conventional lattice dynamics. This treatment has been widely considered in the literature in the case of translational modes. For an extensive discussion on the subject the reader is referred to Wallace's book.[71] Usually, cubic and quartic anharmonic terms are added to the potential and the total energy is then calculated in second-order perturbation. The resulting correction to the harmonic energy is called the anharmonic self-energy. This self-energy is complex and is written as

$$\hbar\Delta\omega(\lambda)=\hbar\Delta(\lambda)-i\hbar\Gamma(\lambda)\,, \tag{3}$$

where λ refers to a mode with a particular wavevector and polarization. The quantity $\Delta(\lambda)$ represents the shift in the phonon frequency and $2\Gamma(\lambda)$ is the full width at

TABLE VIII. Temperature dependence of the frequency and linewidth of the E_g line in the α phase.

Sample 5			Sample 6		
T (°K)	Frequency (cm^{-1})	Full width at half-intensity (cm^{-1})	T (°K)	Frequency (cm^{-1})	Full width at half-intensity (cm^{-1})
38.6	32.5±0.3	10.0(12.0)	38.9	32.5±0.3	9.7(12.6)
35.9	33.1±0.3	8.5(10.4)	36.0	33.1±0.3	8.0(10.8)
32.9	33.7±0.3	6.5(8.4)	32.9	33.7±0.3	6.3(9.0)
29.8	34.1±0.2	5.0(6.6)	29.4	34.0±0.2	4.7(7.4)
26.9	34.4±0.2	3.7(5.1)	26.8	34.3±0.2	3.7(6.2)
24.6	34.5±0.2	2.7(4.2)	24.2	34.6±0.2	2.8(5.0)
21.0	a	1.8(2.6)	20.9	34.8±0.1	1.9(3.2)
17.0	a	0.8(1.6)	17.1	34.9±0.1	1.0(2.2)
12.7	34.95±0.1	0.4(1.2)	12.7	34.95±0.1	0.3(1.2)
9.8	34.95±0.1	0.2(0.9)	9.7	35.0±0.1	0.2(0.9)
5.0	35.0±0.1	0.1(0.6)	5.0	35.0±0.1	0.1(0.6)

[a]These frequencies could not be obtained owing to irregularities in the chart recorder.