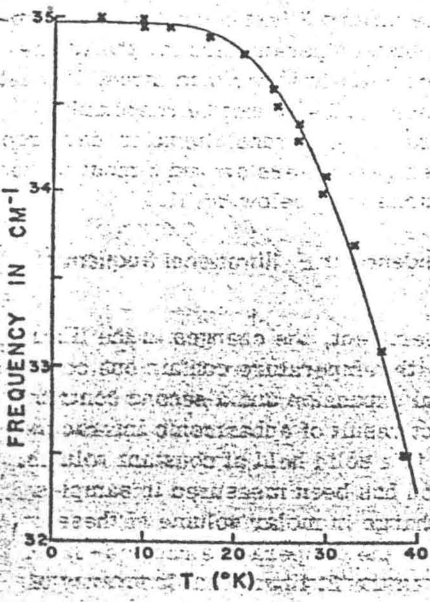

FIG. 8. Temperature dependence of the E_g librational frequency of the α phase: ×, experimental points from samples five and six; ——, best fit to the function in (6).

half-intensity of the corresponding Raman line. In second-order perturbation both cubic and quartic anharmonic terms contribute to $\Delta(\lambda)$ while only cubic terms contribute to $\Gamma(\lambda)$.

The frequency shift is given by[71]

$$\Delta(\lambda)=C(\lambda)+\sum_{\lambda'} C(\lambda,\lambda')n(\lambda'), \tag{4}$$

where $C(\lambda)$ and $C(\lambda,\lambda')$ are temperature independent factors depending only on the strengths of the cubic and quartic anharmonic interactions and on the crystal configuration. The factor $n(\lambda')$ is the average occupation number given by

$$n(\lambda')=\{\exp[\hbar\omega_0(\lambda')/kT]-1\}^{-1}, \tag{5}$$

where $\omega_0(\lambda')$ refers to the harmonic frequency. For the simple case when the E_g libron strongly interacts only with one other excitation, the E_g frequency can be written as

$$\omega(E_g)=\omega_1(E_g)+\omega_2(E_g)\{\exp[\hbar\omega_0(\lambda')/kT]-1\}^{-1}. \tag{6}$$

The data points from Table VIII were fitted to a function of the form given by (6). The best fit, shown in Fig. 8 by the solid line, was obtained with $\omega_1(E_g)=34.97$ cm^{-1}, $\omega_2(E_g)=-51.9$ cm^{-1}, and $\omega_0(\lambda')=83$ cm^{-1}. The error in the frequency $\omega_0(\lambda')$ was estimated at ± 12 cm^{-1}.

This characteristic frequency around 83 cm^{-1} seems too high to represent the excitation of other *librons* to interact with the E_g libron. A more reasonable explanation is that the E_g librons are interacting with phonons. In particular, the infrared-active T_u phonon with an anomalous width has a zero pressure frequency of 70 cm^{-1} which, when extrapolated to a molar volume of 26.2 cm^3/mole assuming a Grüneisen gamma of 3, results in a frequency of 77 cm^{-1}. This value is close to 83 cm^{-1}, indicating that the frequency dependence of the E_g line can be explained if the E_g librons are interacting only with T_u phonons through quartic anharmonicity. It should be mentioned at this point that Mandell[50] has shown that libron–phonon interactions have an important effect in the multipole expansion of the anisotropic intermolecular potential.

The quadrupolar interaction potential has been used in Monte Carlo calculations for classical free rotors[48] resulting in qualitatively the wrong temperature dependence for the librational frequencies in the α-phase. Self-consistent calculations[49] with a 6–12 atom–atom potential yield the correct temperature dependence but the calculated frequency changes are substantially lower than the measured changes.

At this point, a brief excursion is taken back to γ-N_2 and the strong temperature dependence of the B_{1g} frequency. The B_{1g} frequencies were fitted to the function given in (6), resulting in a characteristic frequency $\omega_0(\lambda')=62$ cm^{-1}. Although the fit is inaccurate due to the small number of data points, it would be interesting to measure the frequency of the infrared active E_u phonon. However, theoretical calculations[36,68] result in E_u frequencies of 64.4 and 66.1 cm^{-1} at 4 and 4.5 kbar, indicating that the B_{1g} librons might indeed couple to E_u phonons.

D. Temperature dependence of the linewidth of the E_g line in the α phase

The true linewidth of the E_g line in the α phase is given in Table VIII at several temperatures. The linewidth in (not in) parentheses were obtained assuming that both the instrumental profiles and the true line shape are given by Gaussian (Lorentzian) curves.

The imaginary part of the self-energy in Eq. (3), which is related to the linewidth of a Raman line, is given by[71]

$$\Gamma(\lambda)=\frac{18\pi}{\hbar^2}\sum_{\lambda'\lambda''}|\phi(\lambda,\lambda',\lambda'')|^2\{[n(\lambda')+n(\lambda'')+1]\delta[\omega_0(\lambda)-\omega_0(\lambda')-\omega_0(\lambda'')] + [n(\lambda')-n(\lambda'')][\delta(\omega_0(\lambda)+\omega_0(\lambda')-\omega_0(\lambda''))-\delta(\omega_0(\lambda)-\omega_0(\lambda')+\omega_0(\lambda''))]\}, \tag{7}$$

where $\phi(\lambda,\lambda',\lambda'')$ is related to the cubic anharmonic term in the potential. Wallis, Ipatova, and Maradudin[72] also considered quartic anharmonic contributions in higher-order perturbation. Their result has been simplified by Gervais, Piriou, and Cabannes,[73] who assumed that the phonon under investigation decays into two or three phonons having frequencies which are dispersed around an average. The result is given by

$$\Gamma(\lambda)=\Gamma_1(\lambda)[n(\omega_1)+\tfrac{1}{2}]+\Gamma_2(\lambda)\{[n(\omega_2)+\tfrac{1}{2}]^2+\tfrac{1}{12}\}, \tag{8}$$