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Lattice dynamics of solid N₂ with an *ab initio* intermolecular potential^{a)}

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We have performed harmonic and self-consistent phonon lattice dynamics calculations for α and γ N₂ crystals using an intermolecular potential from *ab initio* calculations. This potential contains electrostatic (multipole) interactions, up to all R^{-9} terms inclusive, anisotropic dispersion interactions up to all R^{-10} terms inclusive, and anisotropic overlap interactions caused by charge penetration and exchange between the molecules. The lattice constants, cohesion energy, the frequencies of the translational phonon modes and the Grüneisen parameters for the librational modes are in good agreement with experimental values, confirming the quality of the potential. The frequencies of the librational modes and those of the mixed modes are less well reproduced, especially at temperatures near the α - β phase transition. Probably, the self-consistent phonon method used does not fully account for the anharmonicity in the librations.

I. INTRODUCTION

During the past several years, a considerable number of experimental and theoretical investigations (see Ref. 1 and references therein) have been made of the molecular motions and intermolecular potentials in solid nitrogen as one of the simplest molecular crystals. Lattice dynamics studies have been performed, mostly because they are considered to be very critical tests of model potentials, since the phonon excitations in solids are much more sensitive for the details of the intermolecular potential than gas phase properties. All the potentials have been semiempirical, i. e., they have been based on simplified models, especially for the short range forces but also for the anisotropic long range interactions, and the parameters have been fitted to the experimental data. Here, we present, for the first time, lattice dynamics calculations for the ordered low temperature α and γ phases of solid N₂, starting from an anisotropic intermolecular potential from *ab initio* calculations.^{2,3}

One has to remember that the accuracy by which the experimental lattice mode frequencies can be reproduced depends not only on the quality of the potential used, but also (sometimes critically) on the method (approximations) employed to solve the dynamics of the crystal. Therefore, we have applied the harmonic model,⁴ as well as the self-consistent phonon procedure⁵ which corrects for the effects of anharmonicity in the potential. So this work can be regarded both as a check on the calculated N₂-N₂ potential and as a test of the approximations commonly used in lattice dynamics studies of molecular crystals.

II. METHODS AND POTENTIAL

The harmonic⁴ and self-consistent phonon⁵ treatments of the lattice vibrations in molecular crystals have been

described in detail elsewhere. Before solving the harmonic dynamical equations, we have minimized the lattice energy for the given potential as a function of the lattice constants, as required theoretically.⁴ The self-consistent phonon (SCP) method is one way to correct for the effects of the anharmonicity in the potential. This method uses a harmonic model with effective force constants that are derived by minimizing the first order expression of the free energy for the actual potential employed. These force constants are calculated as the second derivatives of the potential averaged over the molecular displacements; the latter are described by the displacement-displacement correlation function. Since this function depends on the lattice mode frequencies and eigenvectors, which are related to the force constants via the dynamical equations, the calculations have to be carried out self-consistently. The free energy is minimized also with respect to the lattice constants (and the molecular orientations in the unit cell if these are not fixed by symmetry, as in nitrogen).

The SCP method has been applied earlier to α -N₂ with a Lennard-Jones 12-6 atom-atom potential.⁶ Since this method has been formulated for (rare gas) atomic crystals,⁵ which have no librational degrees of freedom, the authors⁶ have actually solved the dynamical equations for the individual N atoms after introducing an intramolecular N-N force constant. They found some deviations of the librational frequencies from experiment, however, which they ascribed to deficiencies in the intermolecular potential (in particular, the lack of quadrupole-quadrupole interactions). The SCP method which we have applied is a generalization⁷ of the original formalism,⁵ which does explicitly include the librational motions of the molecules, but assumes (in the kinetic energy expression and in the displacement-displacement correlation function) that the amplitudes of the librations are relatively small.

The angle dependent N₂-N₂ potential on which our lattice dynamics calculations are based has been obtained from *ab initio* calculations.^{2,3} It includes the long range electrostatic (multipole-multipole) interactions (all R^{-5} , R^{-7} , and R^{-9} terms), the dispersion interactions (all R^{-6} , R^{-8} , and R^{-10} terms), and the short

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TABLE I. Atom-atom potential fitted to *ab initio* results (Ref. 2). Force centers i have positions $+Z_i$ and $-Z_i$ on the N-N axes (different for each contribution, in principle).

Contributions	Parameters	Potential A	Potential B
Electrostatic	Charges ^a $q_+ = -q_-$	0.373	0.373
$q_i q_j r_{ij}^{-1}$	Positions ^b Z_+, Z_- [Å]	0.847, 1.044	0.847, 1.044
Overlap	A (kJ/mol)	770 000	770 000
$A \exp(-Br_{ij})$	B (Å ⁻¹)	4.037	4.037
	Positions ^b Z_O (Å)	0.547	0.547
Dispersion	C (kJ Å ⁶ /mol)	1407	1511
$C r_{ij}^{-6}$	Positions ^b Z_D (Å)	0.547	0.471

^aIn unit charges $e = 1.602 \cdot 10^{19}$ C.

^bNuclear positions are $Z_N = \pm 0.547$ Å.

range (overlap) forces arising from charge penetration (electrostatic effects) and exchange (Pauli repulsion). The induction (multipole-induced multipole) interactions, which would lead to the largest deviations from a pair-wise additive intermolecular potential,⁸⁻¹⁰ are negligibly small for N₂.^{2,3} The remaining three-molecule interactions, in which the long range triple-dipole dispersion energy and the short range exchange contributions are the dominant terms, are estimated to be only a few percent of the pair energies in the range of the van der Waals minimum.^{10,11}

If one expands the angular dependence of our N₂-N₂ potential in spherical harmonics describing the rotations of the individual molecules (A and B), one finds that the anisotropic dispersion interactions are important up to $L_A = L_B = 2$ inclusive, while the electrostatic and overlap contributions have to be taken up to $L_A = L_B = 4$ inclusive.^{2,3} For comparison, the most extensive and probably the best empirical potential¹ used in N₂ crystal studies only contains isotropic ($L_A = L_B = 0$) dispersion interactions and quadrupole-quadrupole ($L_A = L_B = 2$) electrostatic contributions. We have not used the spherical expansion of the potential in the present lattice dynamics calculations, however, but instead we have applied an atom-atom $\exp - 6 - 1$ potential with the parameters fitted to the *ab initio* results. It has been shown² that, in the case of N₂, the atom-atom (or rather site-site) model yields a fairly good representation of the intermolecular potential, even in describing its angular dependence. It is necessary to use two positive and two negative charges (symmetrically) placed on the N-N axis for representing the electrostatic multipole interactions and, preferably, slightly shifted force centers for the dispersion interactions, too. The site-site potentials with the dispersion centers on the nuclei and with shifted centers have been named potentials A and B, respectively; the parameters are listed in Table I (cf. Table III of Ref. 2).

The lattice dynamics calculations have been made for α -N₂ assuming the space group $Pa3(T_h^6)$,¹² including 54 neighboring molecules in the lattice sums for the (free) energy and the force constants. Only a single lattice

constant (a) had to be optimized for this cubic phase. For the γ phase, which is stable under pressures above 3.5 kbar, the space group is $P4_2/mnm(D_{4h}^{14})$ ¹³ and we have taken 42 neighboring molecules into account; two lattice parameters (a and c) had to be optimized due to the tetragonal symmetry. The SCP program developed by Wasiutynski⁷ has been adapted to these α and γ lattice symmetries; there are four and two molecules per unit cell, respectively. For the calculations under pressure we have used the procedure prescribed by Pawley *et al.*¹⁴ for the harmonic model and we have minimized the Gibbs free energy instead of the Helmholtz quantity in the SCP method.⁷

III. RESULTS

The results calculated for the lattice constants, the cohesion energy, and the frequencies of various phonon modes are listed in Tables II and III for the α and γ phases, respectively, at zero pressure and 4 kbar. They can be compared with the experimental data^{13,15-17} included in these tables. Phonon frequencies have been measured by inelastic neutron scattering in α -N₂ at 15 K¹⁶ and by Raman spectroscopy in γ -N₂ at 4.2 K;¹⁷ The SCP calculations have been performed at the same temperatures. We have also included the results obtained by Raich and Gillis¹ with their recommended empirical potential (1), but not the earlier semiempirical calculations as these were extensively discussed by the latter authors.

Our calculated lattice constants and cohesion energy are in good agreement with the experimental data. Raich and Gillis¹ have used these quantities, for the α phase, as fitting data for their potential, but the present calculations do not contain such fitting procedures, since the potential is entirely determined *a priori*. The lattice mode frequencies from the harmonic calculations are always higher than the experimental values, except for the librational B_{1g} mode in the γ phase. Potential B, which has a somewhat smaller anisotropy in the dispersion interactions (the force centers are closer) than potential A, yields slightly higher frequencies in particular for the librational (the g modes at the Γ point in the Brillouin zone and the R^+ modes at the R points) and mixed (M point) modes. This seems contradictory, but it must be remembered that the anisotropy in the dispersion interactions in fact reduces the larger anisotropy in the electrostatic quadrupole interactions.³

The SCP formalism, which we have only applied with potential A since it is very (computer) time consuming, consistently lowers the frequencies. This can be understood, since the effective potential, averaged over the molecular displacements, is softer than the bare potential at the van der Waals minimum.⁷ This lowering brings the frequencies of the translational modes (u modes at Γ and R^- modes at R) into excellent agreement with experiment. The librational and mixed mode frequencies remain substantially too high, however, although the anharmonic SCP corrections are always in the right direction (except for the γ phase B_{1g} frequency which is somewhat too low already). In principle, this might be due to the potential still not having the correct

TABLE II. α -N₂ crystal data at zero pressure and $T=15$ K.

	Experiment ^a	Semiempirical calculations, ¹ harmonic potential (1)	Present calculations		
			Harmonic		SCP
		Potential A	Potential B	Potential A	
Lattice constant a (Å)	5.644	5.644 ^c	5.644	5.611	5.796
Lattice energy ^b (kJ/mol)	6.92	6.92 ^c	6.00	6.43	6.05
Phonon frequencies ω (cm ⁻¹)					
$\Gamma(0,0,0)$					
E_g	32.3	37.5	40.8	42.4	39.5
T_g	36.3	47.7	50.7	52.9	48.5
T_g	59.7	75.2	74.3	77.7	70.3
A_u	46.8	45.9	52.4	52.8	48.8
T_u	48.4	47.7	52.0	52.6	48.4
E_u	54.0	54.0	57.6	58.9	53.5
T_u	69.4	69.5	77.5	78.8	72.0
$M(\pi/a, \pi/a, 0)$					
M_{12}	27.8	29.6	34.7	34.9	32.5
M_{12}	37.9	40.6	45.9	46.4	43.3
M_{12}	46.8	51.8	57.3	59.1	54.0
M_{12}	54.9	59.0	62.5	64.4	58.5
M_{12}	62.5	66.4	69.6	72.3	64.9
$R(\pi/a, \pi/a, \pi/a)$					
R_1^-	33.9	34.4	36.6	37.1	34.2
R_{23}^-	34.7	35.7	38.6	39.2	35.9
R_{23}^-	68.6	68.3	76.3	77.6	71.0
R_1^+	43.6	50.7	55.6	58.1	52.7
R_{23}^+	47.2	57.8	58.3	61.0	55.7

^aFrom Ref. 16; lattice energy from Ref. 15.^bExperimental: heat of sublimation at 0 K.¹⁵ Calculated: lattice energy at 0 K including zero-point motions.^cFitted to experiment in optimization of the potential parameters.TABLE III. γ -N₂ crystal data at 4 kbar and $T=4$ K.

	Experiment ^a	Semiempirical calculations, ¹ harmonic potential (1)	Present calculations		
			Harmonic		SCP
		Potential A	Potential B	Potential A	
Lattice constants					
a (Å)	3.957	3.940	4.052	4.032	4.100
c (Å)	5.103	5.086	5.029	5.000	5.188
Phonon frequencies ω (cm ⁻¹)					
$\Gamma(0,0,0)$					
E_g	55.0	50.5	57.9	60.1	56.5
B_{1g}	98.1	74.8	86.5	89.2	85.2
A_{2g}	...	105.1	109.7	111.2	107.1
E_u	...	58.3	72.0	71.4	69.3
B_{1u}	...	103.1	110.3	113.8	107.4

^aLattice constants from Ref. 13; phonon frequencies from Ref. 17.

TABLE IV. Grüneisen parameters at 8 K for the librational modes in the α and γ phases of solid nitrogen.

Mode	Grüneisen parameters		
	Experiment ^a	SCP calculations, potential A	
α -N ₂	E_g	1.95	2.00
	T_g	1.63	1.90
	T_g	1.68	1.68
γ -N ₂	E_g	2.3	2.28
	B_{1g}	2.3	2.02

^aFor α -N₂ from Ref. 18; for γ -N₂ from Ref. 17.

anisotropy, but it has been argued before¹ that, irrespective of the precise potential used, the librational modes require larger anharmonic corrections than the translational ones (this is related to their larger relative amplitudes). The SCP method, especially the version that we have used which assumes relatively small librational amplitudes (see Sec. II), might be less effective in correcting for the anharmonic effects in the librations.

The best potential of Raich and Gillis¹ with parameters fitted to the experimental data for solid N₂ yields somewhat lower frequencies already in the harmonic approximation and slightly better overall agreement with the experimental data than the harmonic model applied with the *ab initio* potential. Still, some of their librational frequencies are considerably too high also, while other values are lower than the experimental ones (especially the γ phase B_{1g} frequency, which we find too low, is even much lower in their case). It is uncertain whether the anharmonic corrections would systematically improve the quality of their results, as they do in our case.

The remaining discrepancy between the SCP results and the experimental librational frequencies is clearly illustrated in Fig. 1. Here, we have displayed the temperature dependence in the frequency of the lowest librational E_g mode in the α phase.¹⁸ When the α - β transition temperature (35.6 K) is approached, the am-

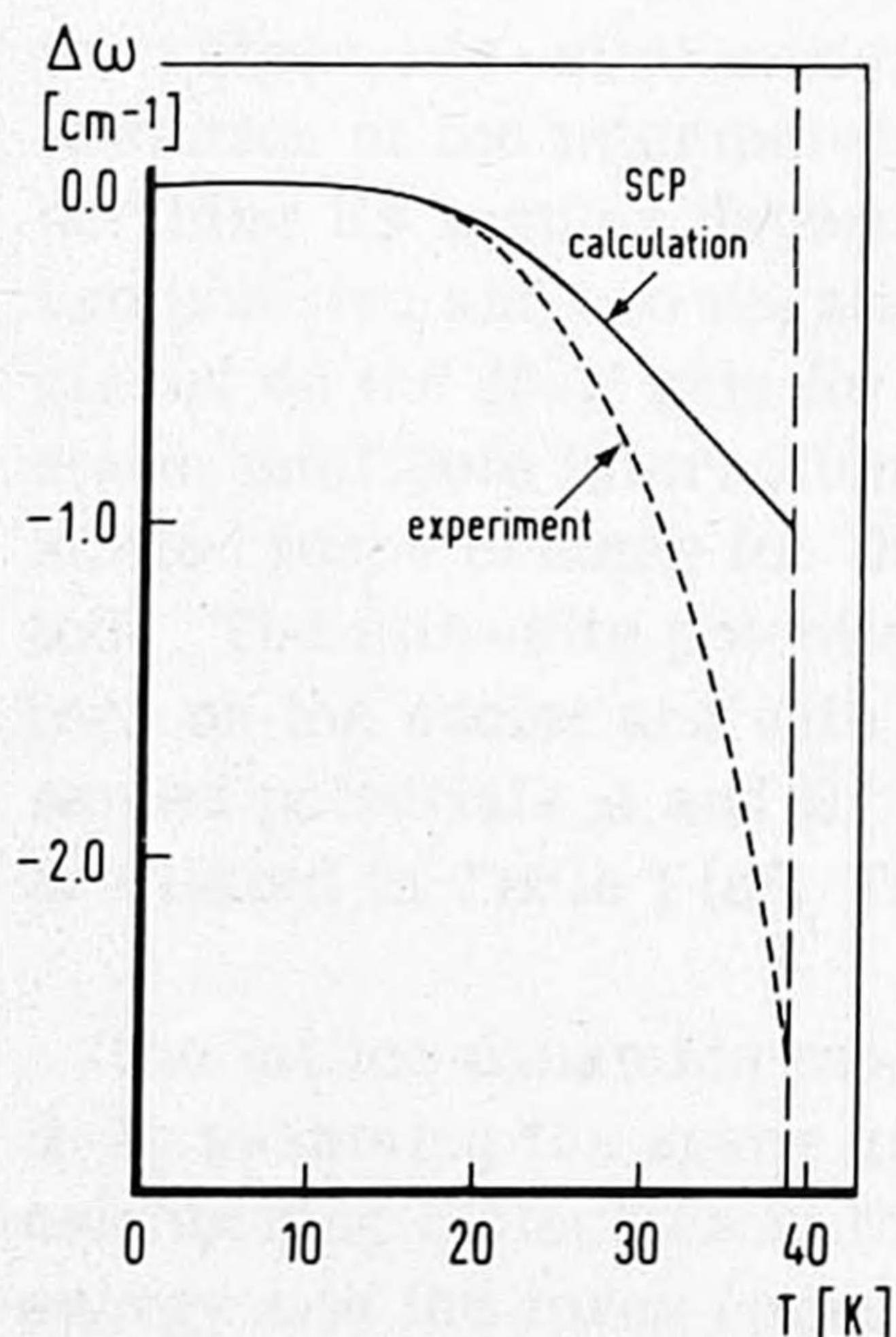


FIG. 1. Temperature dependence of the E_g librational frequency in the α phase. The difference $\Delta\omega$ is defined as $\omega(T) - \omega(T=0)$; experimental data from Ref. 18.

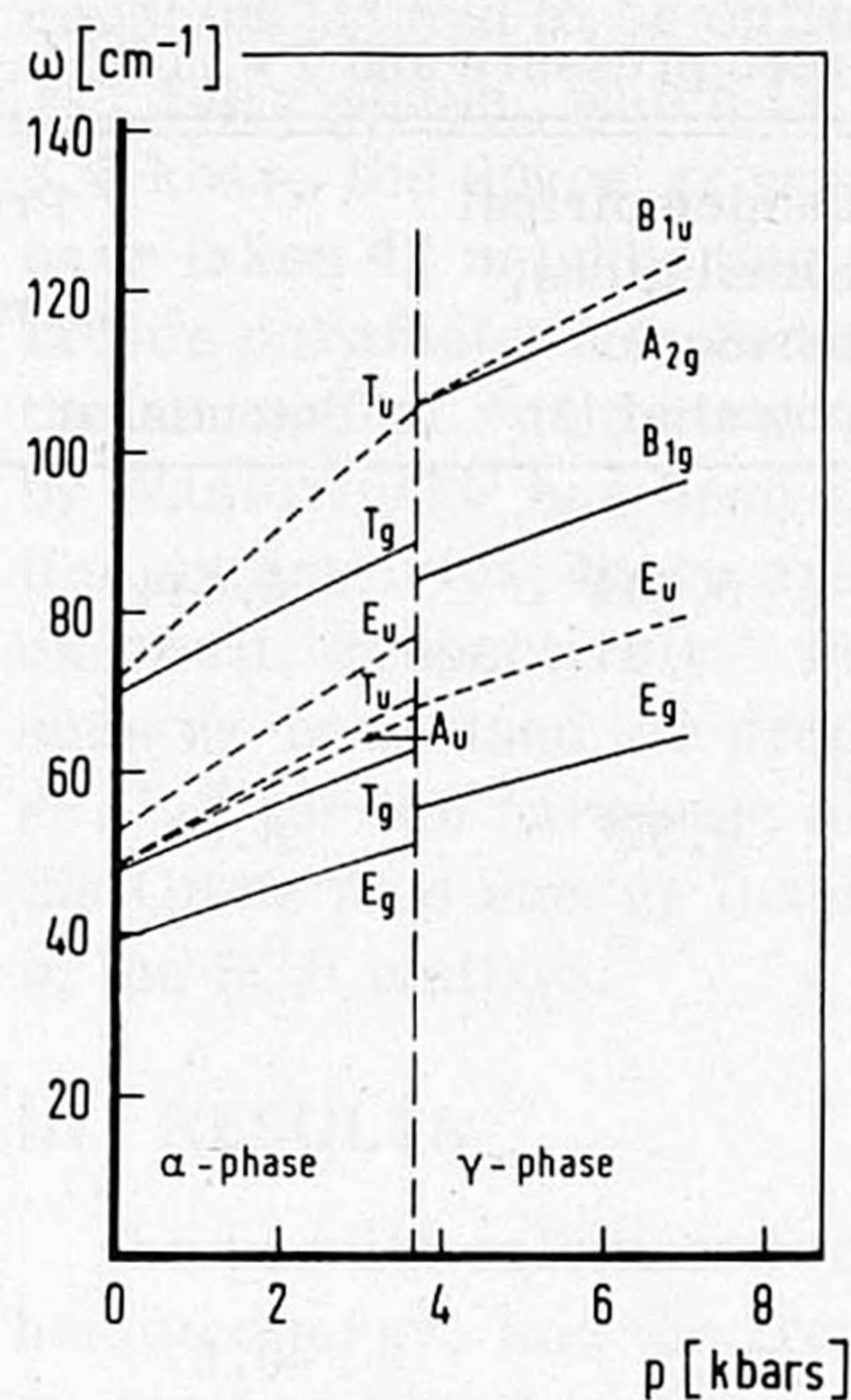


FIG. 2. Pressure dependence of the lattice mode frequencies in the α and γ phases, calculated by the SCP method at 12 K. Closed lines represent the librational modes, and dashed lines the translational ones.

plitudes of libration increase and mode-mode coupling may occur. Apparently, the (present) SCP model cannot completely follow this trend.

In Fig. 2 we have shown the pressure dependence of the $q=0$ mode frequencies (ω_i) at 12 K, calculated by the SCP method. This dependence is related to the molar volume (v) dependence of these modes measured by the Grüneisen parameters

$$\gamma_i = - \left(\frac{\partial \ln \omega_i}{\partial \ln v} \right)_T.$$

So the results presented in Fig. 2 can be indirectly compared with experiment by looking at the Grüneisen parameters that have been measured for the librational frequencies in both the α ¹⁸ and the γ ¹⁷ phase. If the quadrupole-quadrupole interaction would be the only anisotropic contribution to the potential, these parameters would be equal to 5/6. Table IV shows good agreement between the SCP and the measured results at 8 K; this confirms the quality of the anisotropic *ab initio* potential as the Grüneisen parameters are critically dependent on the shape of the potential. The experiment¹⁸ finds the parameters of the α phase to be practically temperature independent, however, whereas the SCP calculations predict a rather strong dependence (see

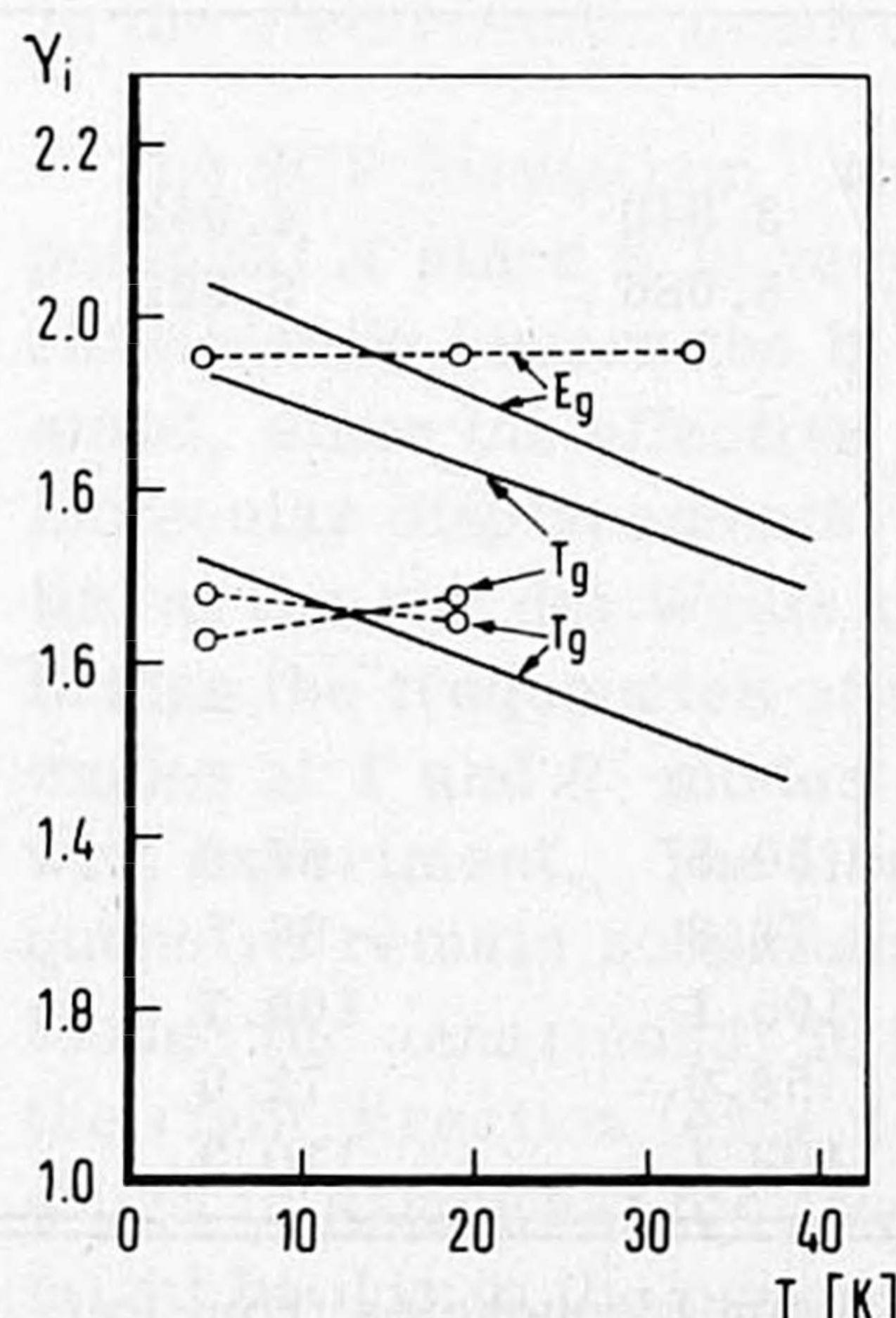


FIG. 3. Temperature dependence of the Grüneisen parameters for the librational modes in the α phase, calculated by the SCP method at zero pressure (closed lines). Experimental values (---o---) from Ref. 18.

Fig. 3). This discrepancy indicates again that the (our) SCP method is not fully capable of reproducing the anharmonic effects occurring in the (α -phase) librations especially at higher temperatures.

IV. CONCLUSIONS

Our lattice structure and dynamics calculations with the *ab initio* N₂-N₂ potential² yield good agreement with experiment for the lattice constants and the translational mode frequencies of α - and γ -N₂ crystals. The anharmonic corrections by the self-consistent phonon method essentially improve the latter. The SCP method also yields good Gruneisen parameters for the librational modes in α - and γ nitrogen at low temperature. Furthermore, the cohesion energy of α -N₂ is rather accurately calculated, especially with the best atom-atom representation of the *ab initio* potential (potential B). So we may conclude that the *ab initio* potential² is quite realistic, both in its radial and angular dependence.

In the librational frequencies some discrepancies with the experimental data remain even in the SCP values, although the anharmonic corrections generally point to the right direction. Apparently, the librational modes have relatively large amplitudes especially in the (low pressure) α phase near the α - β transition temperature, and the SCP method used⁷ cannot completely deal with this case. One should improve on the small amplitude expansion for the librational motions or, possibly, use a quantum mechanical libron treatment¹⁹ in terms of free rotor basis functions instead of the harmonic oscillator basis. In that case, the spherical expansion² of the *ab initio* potential is very useful. Also, classical molecular dynamics (computer simulation) studies of the librational motions in solid N₂²⁰ may be worth trying with the *ab initio* potential² instead of the approximate Lennard-Jones 12-6 atom-atom potential.

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