**Ab initio** description of large amplitude motions in solid N₂. II.
Librons in the β-phase and the α–β phase transition

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Using an *ab initio* pair potential, we have performed mean field and time-dependent Hartree calculations for the reorientational motions in disordered β nitrogen, in a basis of tesseral harmonics. The results show that orientationally localized librational solutions with neighboring molecules rotated over 180° around the crystal c axis are energetically more favorable than (nearly) free precession of the molecules. The experimental symmetry can be obtained by allowing rapid jumps between six equivalent localized states; such a jump model predicts the α–β phase transition at the correct temperature.

I. INTRODUCTION

In the preceding paper I¹ we have described a model for the librations in the ordered α and γ phases of solid N₂. In contrast with the more common (quasi-) harmonic models, this “libron” model holds even for the larger amplitude librations. In the present paper we apply it to the β phase of solid nitrogen where the molecules are orientationally disordered.

Two pictures have been accepted for β-nitrogen and it was not possible from the experimental data²⁻⁸ (x-ray diffraction, neutron scattering, nuclear magnetic resonance, and nuclear quadrupole resonance) to discriminate between these pictures. In both pictures the molecular centers are located on a hexagonal lattice with a c/a ratio close to the ideal hexagonal close packed value. There are two molecules in the unit cell and the space group is P6₃/mmc [see Fig. 1(b) of paper I]. In the first picture the N₂ molecules are freely precessing around the crystal c axis with an angle of 56° ± 2.5° between the molecular axes and the c axis. In the second picture the nitrogen atoms are randomly distributed among 24 equivalent positions of the space group P6₃/mmc with the same angle of about 56° between the molecular axes and the c axis. It has been pointed out,⁴ on the basis of the overlap between specific molecular density contours, that there will probably be some hindrance between neighboring molecules at specific precession angles. This would prevent completely free precessions.

Theoretical treatments of the lattice dynamics in β-nitrogen are not very numerous. This is obviously due to the fact that it is impossible to apply the standard harmonic model. Some authors⁹,¹⁰ have assumed that the intermolecular potential may be averaged over freely rotating N₂ molecules. This yields an effective isotropic potential between N₂ pseudoatoms, which was used in a self-consistent phonon calculation of the translational lattice modes. The reorientational contributions to the free energy were then superimposed, using a free rotor or 12-fold jump model.⁹ Explicit treatments of the reorientational motions on the basis of an anisotropic potential have been given by Mandell¹¹—a classical Monte Carlo simulation with a pure quadrupole–quadrupole interaction—by Klein et al.¹²,¹³—a classical molecular dynamics calculation with atom–atom plus quadrupole–quadrupole potential—and by Dunmore.¹⁴ The latter, quantum mechanical mean-field calculation is similar to the first part of our study and will be discussed below. Optical (infrared, Raman)¹⁵ and inelastic neutron scattering⁵,⁶ studies of the phonon spectrum of β-N₂ are rather scarce as well.

In the present paper we first present a mean-field solution for the reorientational motions in β-N₂ which has the experimentally observed symmetry. When we tried to treat the correlations between the molecular reorientations by means of the time-dependent Hartree (TDH) or the random phase approximation (RPA), the libron frequencies came out purely imaginary, however. It is demonstrated in Sec. II, that this implies the instability of the mean-field solution. So, we have looked for a stable mean-field solution of lower symmetry and calculated the libron frequencies (in Sec. III). Next we discuss the α–β phase transition and the physical picture that emerges for the reorientational motions in β-nitrogen.

II. STABILITY CONDITIONS FOR THE MEAN-FIELD MODEL

It has been demonstrated by Fredkin and Werthamer¹⁶ that the stability of the solutions of the mean-field (MF) or time-independent Hartree equations for lattice dynamics is related to the eigenvalues of the time-dependent Hartree equations. For zero temperature the latter are identical to the RPA equations (see paper I). Imaginary eigenfrequencies of the TDH equations imply that the original MF solution does not correspond to a local minimum of the free energy. The result in the Appendix of Ref. (16) is a generalization to nonzero temperature of the stability conditions for Hartree–Fock solutions in many-fermion systems.¹⁷⁻²⁰ We give a slightly different proof which follows closely the presentation of the theory in paper I.

We start with the thermodynamic variation principle for the Helmholtz free energy:

\[
A_{\text{var}} = A_0 + \langle H - H_0 \rangle_0 \rightarrow A,
\]

(1)
where $H$ is the exact lattice Hamiltonian (omitting the constant term from paper I):

\[ H = \sum \lambda_p (\Omega_p) + \frac{1}{2} \sum_{p, p'} ^{'} \Phi_{p, p'} (\Omega_p, \Omega_{p'}) \tag{2} \]

and $H_0$ may be any Hamiltonian. The thermodynamic expectation value $\langle X \rangle_0$ is defined as

\[ \langle X \rangle_0 = \text{Tr}(D_0 X), \tag{3} \]

where $D_0 = \sum \lambda_{p, p'} e^{-\beta H_{p, p'}}$ is the density operator associated with the approximate Hamiltonian $H_0$ and $A_0$ is the corresponding free energy:

\[ A_0 = -\beta^{-1} \ln Z_0. \tag{4} \]

The partition function reads

\[ Z_0 = \text{Tr}(e^{-\beta H_0}) \tag{5} \]

and $\beta = (k_B T)^{-1}$. The exact quantities are given by

\[ A = -\beta^{-1} \ln Z \] with

\[ Z = \text{Tr}(e^{-\beta H}). \tag{11} \]

The MF or Hartree equation will be found by defining $H_0$ as a sum of one-particle operators:

\[ H_0 = \sum \lambda_p (\Omega_p), \tag{6} \]

from which it follows that

\[ D_0 = \prod_p d_{p, p'} (\Omega_p) \tag{7} \]

with

\[ d_{p, p'} (\Omega_p) = (Z_{p, p'}^{-1} e^{-\beta H_{p, p'}} (\Omega_p), \tag{8} \]

\[ Z_{p, p'} = \text{Tr}(e^{-\beta H_{p, p'}} (\Omega_p)) \tag{12} \]

and making $A_{\text{var}}$ stationary with respect to variations of $H_0$:

\[ H_{p, p'} (\Omega_p) = H_{p, p'} (\Omega_p) + H_p (\Omega_p). \tag{9} \]

In order to derive the effect of such variations on the free energy, we use the following well-known expansion

\[ e^{-\beta H_{p, p'} + \beta h} = e^{-\beta H_p} T \exp \left[ -\int_0^h db \, \hat{h}_p (b) \right] \tag{13} \]

\[ = e^{-\beta H_p} \left[ 1 - \int_0^h db \, \hat{h}_p (b) + \int_0^h db_1 \int_0^{b_1} db_2 \, \hat{h}_p (b_1) \hat{h}_p (b_2) - \ldots \right] \tag{14} \]

with

\[ \hat{h}_p (b) = e^{\beta H_p} h_p e^{-\beta H_p}, \tag{15} \]

where $T$ is the Dyson time-ordering operator, acting here on the inverse temperatures $\beta_1, \beta_2$, etc. In order to simplify the notation we have stopped indicating the dependence of all quantities on $\Omega_p$. Expanding the logarithm in Eq. (4) we obtain for the first order variation in $A_0$:

\[ A_{\text{var}} = -\beta^{-1} \sum_p \left( \int_0^h db_1 \int_0^{b_1} db_2 \, \hat{h}_p (b_1) \hat{h}_p (b_2) \right)_p \tag{16} \]

The single-particle expectation value is defined as

\[ \langle x_p \rangle_p = \text{Tr}(d_p^{MF} x_p), \tag{17} \]

with $d_p^{MF}$ given by Eq. (8).

The same variation (9) of $H_{p, p'}^{MF}$ by $h_p$ makes the corresponding density operator vary as

\[ d_p = e^{-\beta (H_{p, p'}^{MF} + h_p) / T} \text{Tr}(e^{-\beta (H_{p, p'}^{MF} + h_p)}) \tag{18} \]

with

\[ \delta_0 = d_p^{MF} + \delta_0^{(1)} + \ldots \tag{19} \]

It is easy to verify that $\text{Tr}(d_p^{MF} | \delta_0^{(1)}) = 0$. The same result holds for the higher order terms, so that the density operator remains normalized, $\text{Tr}(d_p^{MF} | \delta_0^{(1)}) = 1$, in every order. For the first order variation of $A_{\text{var}}$ we find the following expression:

\[ A_{\text{var}} = A_0^{(1)} + \sum_p \text{Tr}(d_p^{MF} h_p) + \sum_{p, p'}' \text{Tr}(d_p^{MF} \Phi_{p, p'}) \tag{20} \]

\[ - \sum_p \text{Tr}(d_p^{MF} H_p^{MF}) - \sum_p \text{Tr}(d_p^{MF} h_p). \tag{21} \]

Substituting Eqs. (12) and (13), we observe immediately that the first term cancels the last term. Putting $A_{\text{var}}^{(1)} = 0$ for arbitrary variations $\delta_0^{(1)}$, which are related to the variations $h_p$ via Eq. (15), we obtain the MF result

\[ H_p^{MF} = L_p + \sum_p \text{Tr}(d_p^{MF} \Phi_{p, p'}) \tag{22} \]

\[ = L_p + \Phi_p^{MF}. \tag{23} \]

In order to investigate whether the MF solution corresponds to a local minimum of $A_{\text{var}}$, we must look at the second order variation $A_{\text{var}}^{(2)}$. All quantities occurring in $A_{\text{var}}$ can be expanded via Eq. (10), now taken up to the second order terms inclusive. Expanding the logarithm in Eq. (4) again, we get

\[ A_{\text{var}}^{(2)} = \beta^{-1} \sum_p \left( \int_0^h db_1 \int_0^{b_1} db_2 \, \hat{h}_p (b_1) \hat{h}_p (b_2) \right)_p \tag{24} \]

\[ - \frac{1}{2} \left( \int_0^h db_1 \, \hat{h}_p (b_1) \right)_p \tag{25} \]

\[ = \beta^{-1} \sum_p \int_0^h db_1 \int_0^{b_1} db_2 \, \hat{h}_p (b_1) \hat{h}_p (b_2) \tag{26} \]

\[ + \frac{1}{2} \beta \sum_p \langle h_p \rangle_p^2. \tag{27} \]

The total second order variations in $A_{\text{var}}$ can then be written as

\[ A_{\text{var}}^{(2)} = A^{(2)}_0 + \frac{1}{2} \sum_{p, p'}' \text{Tr}(d_p^{MF} \delta_0^{(1)} \Phi_{p, p'}) \tag{28} \]

\[ + \sum_p \text{Tr}(d_p^{MF} L_p) + \frac{1}{2} \sum_{p, p'}' \text{Tr}(d_p^{MF} \delta_0^{(2)} d_p^{MF} \Phi_{p, p'}) \tag{29} \]

\[ - \sum_p \text{Tr}(d_p^{MF} | \delta_0^{(1)} h_p). \tag{30} \]

The terms with $\delta_0^{(2)}$ cancel after substituting the MF Hamiltonian (17) and the remaining terms...
\[ A^{(2)}_{\text{var}} = A^{(2)}_{0} + \frac{1}{2} \sum_{p,p'} \text{Tr} \{ \delta^{(p)}(E^{(p)}) \delta^{(p')}(E^{(p')}) \Phi_{p,p'} \} \]
\[ - \sum_{p} \text{Tr} \{ \delta^{(p)}(h_{p}) \} \]

can be worked out by substituting Eqs. (15) and (18). Taking the traces with respect to the eigenstates \( |\alpha_{p}\rangle = |\psi_{p}^{(a)}\rangle \) of the MF Hamiltonian

\[ H^{MF}_{p} |\alpha_{p}\rangle = \epsilon^{(a)} |\alpha_{p}\rangle, \]

it is not difficult to obtain the result

\[ A^{(2)}_{\text{var}} = \frac{1}{2} \sum_{p,p'} \sum_{\alpha,\beta,\alpha',\beta'} \langle \alpha,\alpha'|\Phi_{p,p'}|\beta,\beta'\rangle \langle \beta,\beta'|\delta^{(p)}(\alpha_{p}) \rangle \langle \beta,\beta'|\delta^{(p')}|\alpha_{p}\rangle \]
\[ - \frac{1}{2} \sum_{p} \sum_{\alpha,\beta,\alpha',\beta'} \langle \alpha,\alpha'|h_{p}|\beta,\beta'\rangle \langle \beta,\beta'|h_{p}|\alpha_{p}\rangle + \frac{1}{2} \sum_{p} \sum_{\alpha,\beta} \beta P^{(a)}(\alpha_{p}|h_{p}|\alpha_{p})^{2} - \frac{1}{2} \sum_{p} \beta \langle h_{p}\rangle^{2}. \]

The second term has been simplified via interchanging \( \alpha_{p} \) and \( \beta_{p} \). The occupation numbers \( P^{(a)} \) are given by

\[ P^{(a)} = \langle \alpha_{p}|d_{p}^{MF}\alpha_{p}\rangle = e^{-\beta\epsilon^{(a)}} \sum_{\alpha} e^{-\beta\epsilon^{(a)}}. \]

In Eq. (21), and also later, we use the fact that in all our applications the spectra of all \( H^{MF}_{p} \) are equal (see paper I), i.e., \( \epsilon^{(a)} \) does not depend on \( P \). Equation (22) contains both the variations \( h_{p} \) in the MF Hamiltonian and the variations \( \delta^{(p)}(\alpha_{p}) \) in the density operator. Via relation (15) it could be expressed in terms of \( h_{p} \) only, but we find it more convenient to write Eq. (15) in matrix element form:

\[ \langle \alpha_{p}|\delta^{(p)}(\alpha_{p})|\beta_{p}\rangle = \frac{P^{(a)}(\alpha_{p}) - P^{(b)}(\beta_{p})}{\epsilon^{(a)} - \epsilon^{(b)}} \langle \alpha_{p}|h_{p}|\beta_{p}\rangle \quad \text{for} \quad \epsilon^{(a)} \neq \epsilon^{(b)} \]
\[ = -\beta P^{(a)}(\alpha_{p}|h_{p}|\alpha_{p}) - \langle h_{p}|_{\beta_{p}} \rangle \quad \text{for} \quad \epsilon^{(a)} = \epsilon^{(b)} \]

and to use this relation backwards, in order to express Eq. (22) completely in terms of the matrix elements of \( \delta^{(p)} \):

\[ A^{(2)}_{\text{var}} = \frac{1}{2} \sum_{p,p'} \sum_{\alpha,\beta,\alpha',\beta'} \langle \alpha,\alpha'|\Phi_{p,p'}|\beta,\beta'\rangle \langle \beta,\beta'|\delta^{(p)}(\alpha_{p}) \rangle \langle \beta,\beta'|\delta^{(p')}|\alpha_{p}\rangle \]
\[ - \frac{1}{2} \sum_{p} \sum_{\alpha,\beta} \beta P^{(a)}(\alpha_{p}|h_{p}|\alpha_{p})^{2} - \frac{1}{2} \sum_{p} \beta \langle h_{p}\rangle^{2}. \]

The last two sums over diagonal terms in Eq. (22) correspond with the diagonal \( (\alpha_{p} = \beta_{p}) \) terms in the last summation of Eq. (25). These terms have been formally included in this summation via the relation

\[ \lim_{\epsilon^{(a)} \rightarrow \epsilon^{(b)}} \frac{P^{(a)}(\alpha_{p}) - P^{(b)}(\beta_{p})}{\epsilon^{(a)} - \epsilon^{(b)}} = -\frac{1}{\beta P^{(a)}}. \]

Equation (25) is identical to the expression obtained by Fredkin and Werthamer,\(^{16}\) who did not explicitly consider the diagonal terms.

It is easy to adapt this expression to the translational symmetry of the crystal. Defining the first order variations in the symmetry adapted density matrix as variational coefficients:

\[ C(q)_{\alpha,\beta,i} = N^{-1/2} \sum_{n} e^{i\mathbf{q}\cdot\mathbf{R}_{n}} \langle \alpha_{p}|\delta^{(p)}(\alpha_{p})|\beta_{p}\rangle \]

with \( P = \{ n,i \} \), and the Fourier transformed pair interaction matrix:

\[ \Phi(q)_{\alpha,\beta,i;\alpha',\beta',i'} = \sum_{n} e^{i\mathbf{q}\cdot\mathbf{R}_{n}} \langle \alpha_{p}|\alpha'|\Phi_{p,p'}|\beta_{p}|\beta'_{p}\rangle \]

with \( P = \{ 0,i \} \) and \( P' = \{ n,i' \} \), and \( \Phi_{p,p'} = 0 \), just as in paper I, we find that \( A^{(2)}_{\text{var}} \) becomes additive in the wave vector \( q \):

\[ A^{(2)}_{\text{var}} = \sum_{q} A^{(2)}_{\text{var}}(q) \]

J. Chem. Phys., Vol. 81, No. 8, 15 October 1984
and use the relations (30) to (32), we can rewrite Eq. (29) in matrix form:

\[
A_{\text{var}}^{(2)}(q) = \frac{1}{2}
\begin{pmatrix}
(u(q))' & (\Phi(q) - \chi) \\
(v(q))' & (\Phi(q) - \chi)
\end{pmatrix}
\begin{pmatrix}
(u(q)) \\
(v(q))
\end{pmatrix}
\begin{pmatrix}
(\Phi(q) - \chi) \\
(\Phi(q) - \chi)
\end{pmatrix}
\begin{pmatrix}
(w(q)) \\
(w(q))
\end{pmatrix}
\]

with the matrices \(\Phi(q)\), \(\phi(q)\), and \(f(q)\) all being subblocks of the matrix \(\Phi(q)\) in Eq. (28) with \(\{\alpha > \beta, \alpha' > \beta'\}\), \(\{\alpha > \beta, \alpha' = \beta'\}\), and \(\{\alpha = \beta, \alpha' = \beta'\}\), respectively. The diagonal matrices \(\chi\) and \(g\) are defined as

\[
\chi_{\alpha,\beta,\alpha',\beta'} = \delta_{\alpha,\alpha} \delta_{\beta,\beta'} \delta_{\alpha',\alpha'} \frac{\epsilon(\alpha) - \epsilon(\beta)}{\epsilon(\alpha) - \epsilon(\beta)} \quad \text{for} \quad \alpha > \beta,
\]

\[
\delta_{\alpha,\alpha} = -\delta_{\alpha,\alpha} \delta_{\beta,\beta'} \delta_{\alpha',\alpha'} (\epsilon(\alpha) - \epsilon(\beta))^{-1}.
\]

The matrix occurring in Eq. (34) is related to the matrix \(M(q)\) occurring in the TDH equations (cf. paper I) by

\[
M(q) = \begin{pmatrix}
P & 0 & 0 \\
0 & P & 0 \\
0 & 0 & N(q)
\end{pmatrix},
\]

where \(P\) is a diagonal population difference matrix

\[
P_{\alpha,\beta,\alpha',\beta'} = \delta_{\alpha,\alpha} \delta_{\beta,\beta'} \delta_{\alpha',\alpha'} (P^{(\alpha)} - P^{(\beta)})
\]

for \(\{\alpha > \beta, \alpha' > \beta'\}\).

The matrix \(N(q)\) is obtained from the matrix in Eq. (34) by erasing the central rows and columns.

The second variation \(A_{\text{var}}^{(2)}(q)\) is positive for any set of variation coefficients \(\{33\}\) if and only if the matrix in Eq. (34) is positive definite. Via the separation theorem for the eigenvalues of Hermitian matrices and their principal minors\(^2\) it follows then, that its submatrix \(N(q)\) must be positive definite, too. The latter matrix can be blocked by means of a simple similarity transformation \(T\): adding and subtracting its rows and columns, which corresponds with taking the real and imaginary parts of the variation coefficients \(u\) and \(w\) as new variables. This yields:

\[
N'(q) = T^{-1}N(q)T = \begin{pmatrix}
2\Phi(q) - \chi & 0 \\
0 & -\chi
\end{pmatrix}.
\]

The diagonal submatrix \(-\chi\) is clearly positive definite, see Eq. (35). As a result, the matrices \(N'(q)\) and \(N(q)\), and therefore \(A_{\text{var}}^{(2)}\) as given by Eq. (34), can only be positive definite if the submatrix \(2\Phi(q) - \chi\) is positive definite. The latter matrix occurs in the generalized eigenvalue problem, Eq. (20) of paper I, which yields the squares of the TDH frequencies. Multiplying this eigenvalue equation by \(-1\) and using the fact that the metric matrix \(-P^{-1}\chi^{-1}P^{-1}\) is diagonal and positive definite, one easily shows that the squares of the TDH frequencies are all positive if and only if \(2\Phi(q) - \chi\) is positive definite.

In summary, we have proved that the squares of the TDH eigenfrequencies are positive, provided that the mean-field solution corresponds with a local minimum in \(A_{\text{var}}\). So, if one or more of these squares are negative, i.e., if one or more of the TDH frequencies \(A^{(k)}(q)\) are imaginary, then the matrices \(N'(q)\) and \(N(q)\) have negative eigenvalues. Choosing the variation coefficients \(u(q)\) and \(w(q)\) in Eq. (33) as one of the eigenvectors of \(N(q)\) associated with these negative eigenvalues and \(v(q) = 0\) yields a negative value of \(A_{\text{var}}^{(2)}\) and thus a free energy which is lower than the MF value. Inspecting these eigenvectors can help us in finding a more stable MF solution.

### III. MEAN FIELD AND LIBRON CALCULATIONS

The methods applied for the lattice dynamics calculations on \(\beta\)-nitrogen are the same as those used in paper I. Also, we have employed the same \(ab\ initio\ potential\)\(^2\) with the anisotropy expressed in the form of a spherical expansion, including spherical harmonics up to \(l = 6\) on each molecule. We have used the experimental\(^4\) unit cell parameters \(a\) and \(c\) [see Fig. 1(b) of paper I], at zero pressure and temperature 46 K. The mean-field states of the molecules on each lattice site have been expanded in tesseral harmonics with even or odd \(l\) for pure \(ortho\) or \(para\) nitrogen, respectively. Lattice summations over the potential have been extended over eight shells, \(R < 9.87\ \text{Å}\). We have not assumed the mean-field potential to have axial symmetry around the \(c\) axis, as Dunmore\(^1\) has done. For the existence of localized solutions with broken symmetry, see below, the nonaxial components are crucial.

Just as in Paper I we have started by assuming the experimentally observed crystal symmetry. Thus, the two molecules in the hexagonal unit cell have been given identical

![FIG. 1. Calculated mean-field levels for \(\beta\)-nitrogen corresponding with the delocalized (unstable) mean-field states and the (stable) localized states. The arrows, which are the free rotor levels, indicate that the delocalized mean-field spectrum resembles a perturbed rotor spectrum.](image)
Table I. Orientational form factors in $\beta$-nitrogen from mean field calculations, see Eq. (39).

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Delocalized</td>
<td>Localized</td>
</tr>
<tr>
<td>$T = 30$ K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{2,0}$</td>
<td>$-0.027$</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>$C_{4,0}$</td>
<td>$-0.082$</td>
<td>$-0.060$</td>
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<tr>
<td>$C_{6,0}$</td>
<td>$0.029$</td>
<td>$0.020$</td>
</tr>
<tr>
<td>$C_{6,6}$</td>
<td>$-0.016$</td>
<td>$-0.013$</td>
</tr>
</tbody>
</table>

*Converted to normalized tesseral harmonics.
FIG. 3. Orientational probability distribution of the molecular axes for the localized mean-field states in $\beta$-nitrogen, drawn for one molecule in the unit cell; the other molecule in the cell is rotated over $\theta = 180^\circ$. The distribution does not change qualitatively up to (at least) $T = 70$ K; it just becomes slightly wider with increasing temperature. Reading of the contour plot as in paper I, Fig. 3.

The motions of the molecules in this new MF solution can be described as localized librations about equilibrium orientations of the molecular axes which point to one of the square faces of the hexagonal cage, see Fig. 1(b) of paper I. The angle $\theta = 52^\circ$ between the molecular axes and the crystal $c$ axis is slightly smaller than for the delocalized case. The coefficients in the form factor are similar, see Table I. In particular, the coefficient $C_{20}$ is still relatively small, as expected from the experimental data. The much higher excitation energies in the MF spectrum, Fig. 1 right-hand side, and the similarity between the ortho and para nitrogen solutions are typical for localized librations (cf. the $\alpha$ and $\gamma$ nitrogen results in I).

The most remarkable feature of the localized MF states is that the experimentally observed hexagonal symmetry of the crystal is completely lost. This experimental symmetry will be restored if we assume that, for each molecule, six equivalent MF solutions are available, which are related to each other by rotations of $60^\circ$ around the $c$ axis, and that the molecules can jump from one localized solution to another within the time that is characteristic for the observation process (the inverse NMR frequency, for example). We shall digress on this hypothesis in Sec. IV, when discussing the $\alpha$–$\beta$ phase transition. Our jump model thus assumes six localized orientations for each molecule in the unit cell, i.e., 12 molecular positions or 24 atomic positions in each primitive cell. These are not the 24-fold degenerate Wyckoff positions of the space group $P\bar{6}_3/mmc$, however, but two sets of 12-fold degenerate positions. Actually, as observed in Ref. 2, with the molecules in alternate layers packed as they are in the (near) hcp lattice, it is not possible that the atoms occupy just one set of 24-fold degenerate positions. This can easily be seen by checking that the centers of inversion of the space group are not located on the lattice sites occupied by the molecular midpoints.

Next we calculated the libron frequencies by the TDH method with two excited, localized, MF states on each molecule. All these frequencies are real now, as they should be for a stable MF solution. As can be expected from the localized nature of the MF states, we find that the libron frequencies (see Table II) are of similar size as those for the ordered $\alpha$ and $\gamma$ phases, and comparable also with the translational phonon frequencies. The experimental spectra show two very broad peaks of which the higher one around $50$ cm$^{-1}$ (depending on the temperature and pressure) has been interpreted as a libron band and the lower one around $25$ cm$^{-1}$ as a translational phonon band (Table II). The higher libron frequency agrees reasonably well with our results, but according to our calculated frequencies, the libron modes might cause some absorption in the lower band as well (apart from symmetry and intensity considerations, which we have not looked at). Our results indicate that the broadening of the observed libron band is caused by coupling localized librational modes with more or less random jumps in the orientations of the molecules by multiples of $60^\circ$.

IV. THE $\alpha$–$\beta$ PHASE TRANSITION

In Fig. 4 we have plotted the free energy $A_{\text{var}}$ calculated from the different MF solutions of $\alpha$ and $\beta$ nitrogen, accord-

<table>
<thead>
<tr>
<th>Calculated (libron)</th>
<th>Experiment</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TDH</td>
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<tr>
<td>Temperature (K)</td>
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<tr>
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<td>28.26</td>
</tr>
<tr>
<td>Molar volume (cm$^3$ mol$^{-1}$)</td>
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<tr>
<td>Frequencies</td>
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<td>65.7</td>
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<td>73.3</td>
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* As quoted in Ref. 15.
FIG. 4. Free energy (at zero pressure) for \( \alpha \)-nitrogen (see paper I) and \( \beta \)-nitrogen, in different mean-field models (closed lines). The dashed free rotor curve has been calculated from the isotropic \((l,l,l) = (0,0,0)\) term of the \textit{ab initio} potential (Ref. 23) by adding the free rotor expression for the free energy, as in Ref. 9. The dashed jump model curve has been obtained from the localized mean-field solution (with the full anisotropic potential) by adding an entropy term \(-k_B T \ln 6\) (see the text).

Our jump model seems related to the 12-fold jump model invoked by Raich \textit{et al.}\cite{23}, who have also used their model to study the \( \alpha-\beta \) phase transition. However, our results show that it is essential that the jumps occur between localized librational states of the molecules which lie in deep wells that can only be obtained from the full anisotropic potential. Raich \textit{et al.}\cite{23} have used an effective, orientationally averaged, isotropic potential, which in our case would produce a free energy curve close to the free rotor curve. So the physical picture for \( \beta \)-nitrogen that emerges is that of a sixfold jump model between orientationally localized librational states of the molecules. The entropy of the crystal can be assumed to be the sum of two contributions. The first part originates from the librations of the molecules around their equilibrium orientations and it is approximately the entropy calculated in the localized mean-field model. The second part is due to the distribution of the molecules over their six positions. Although the latter distribution is strongly correlated, it is in the spirit of the present MF approach to put the corresponding entropy equal to \(-k_B T \ln 6\). The free energy per particle will thus be equal to the result of the localized model, minus \(k_B T \ln 6\). This yields the dashed curve in Fig. 4 marked "\( \beta-N_2 \) jump". This curve crosses the free energy curve for \( \alpha-N_2 \) at \( T = 34\text{ K} \), in close agreement with the experimental \( \alpha-\beta \) phase transition temperature, \( T = 35.6\text{ K} \).

In principle, one could suggest that the same type of jumps occur between four equivalent localized solutions in \( \alpha-N_2 \), with the molecules oriented along one of the body diagonals of the cubic lattice (see paper I). One can argue, however, that such jumps of the individual molecules are energetically much more unfavorable in \( \alpha-N_2 \) than they are in \( \beta-N_2 \). The strongest indication for this is the experimentally observed crystal symmetry which agrees with the symmetry of a specific localized MF solution for \( \alpha-N_2 \). Further arguments can be found from the MF calculations themselves. In the first place, the overlap between the sixfold localized MF states in \( \beta-N_2 \) is substantially larger than the overlap between the four states in \( \alpha-N_2 \) and, therefore, tunneling will be faster in \( \beta-N_2 \). Secondly, we have tried to generate delocalized solutions for \( \alpha-N_2 \) by forcing all four molecules in the unit cell to have identical MF states as in the delocalized \( \beta-N_2 \) model. The molecules in \( \alpha-N_2 \) remain still localized, however, with their axes oriented along one of the cube edges. So, even at the expense of a substantial amount of lattice energy, the molecules in \( \alpha-N_2 \) will not reorient themselves as in \( \beta-N_2 \). Apparently, the rotation barriers are substantially higher in \( \alpha-N_2 \) than they are in \( \beta-N_2 \). A definite theoretical confirmation of the jump model in \( \beta-N_2 \) must wait for a sound theoretical formulation of the dynamics of this model, though.

Our jump model seems related to the 12-fold jump model invoked by Raich \textit{et al.}\cite{23}, who have also used their model to study the \( \alpha-\beta \) phase transition. However, our results show that it is essential that the jumps occur between localized librational states of the molecules which lie in deep wells that can only be obtained from the full anisotropic potential. Raich \textit{et al.}\cite{23} have used an effective, orientationally averaged, isotropic potential, which in our case would produce a free energy curve close to the free rotor curve. So the physical picture for \( \beta-N_2 \) that emerges is that of a sixfold jump model between orientationally localized librational states of the molecules.
There is a tendency for neighboring molecules to stay 180° out of phase, in order to achieve a favorable lattice energy. Thus, it is clear that an appropriate quantum dynamical model for the jump process, which is still to be developed, must include the intermolecular (pair) correlations from the outset.

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