Microscopic theory of phase transitions in $NaNO_2$

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The energy levels and the wave functions of nitrite groups (NGs) in the crystal potential of $NaNO_2$ are determined and used to construct a four-dimensional representation of the Hubbard operators for the NGs. The Born–Mayer and dipole-dipole interactions between the NGs are projected into the Hubbard-operator representation and the Hamiltonian of the system is constructed taking into account the coupling of the NGs with the translational degrees of freedom. Based on this a quantitative phase diagram of the crystal is obtained in the temperature-pressure plane. The dependence of the wave vector of the incommensurate phase on the temperature, pressure, and dipole moment of NGs are also found.

INTRODUCTION

In Ref. 1 we proposed a microscopic theory of phase transitions (PTs) in alkali-metal cyanides taking into account the short-range repulsive interactions between the metal ions and the atoms of the cyanogen groups as well as the elastic and dipole-dipole interactions. The theory is based on the finite-dimensional representations (Hubbard operators), constructed on the basis of the characteristic functions of the cyanogen groups, rotating in a multiminimum potential produced by the metal ions. As a result, using the empirical interatomic interaction constants and the elastic constants as the starting data we were able to determine the entire sequence of PTs and the type of ordering in each phase.

In the present paper this theory is applied to $NaNO_2$. A quite complete qualitative understanding of the nature of the PT into the incommensurate (*IC*) phase in $NaNO_2$ was attained in Refs. 2–4. It was shown that the incommensurate phase results from the combined effect of the dipole-dipole interactions of the NO_2 groups (NGs) and the short-range interactions of the atoms in the NGs with the nearest metal ions. Another important circumstance with which the *IC*-phase is associated is the form of the ordering molecule itself, more accurately, the relative geometry of molecular structures in the unit cell, to which Heine and McConnell drew attention.[5] Indeed, all these interactions also occur in alkali-metal cyanides, which, nonetheless, do not exhibit an *IC*-phase. The difference between $NaNO_2$ and, say, KCN lies in the form of the ordering molecular group NO_2, which has the form of a triangle (Fig. 1); this changes its placement in the unit cell as compared with the CN-group in KCN.

The phase-transition temperature, the wave vector, and the temperature interval in which the *IC*-phase exists in $NaNO_2$ were determined on the basis of the Ising model,[6] in which the NGs are regarded as interacting dipoles, occupying in the paraelectric phase with equal probability the $\pm\mathbf{b}$ directions (Fig. 1) in a rigid lattice. As will be shown in this paper, however, in order to give a complete quantitative description of PTs in $NaNO_2$ a four-level description of the NGs is needed. In addition, the standard pseudospin description ignores the change in the equilibrium positions of the Na^+ ions and the NGs relative to one another, as was done in Refs. 7 and 8. These displacements are important because they induce elastic dipoles, whose interaction makes a significant contribution to the *IC*-phase. In Ref. 8 the strong correlations between the orientations of the NGs and the positions of the metal ions nearest to them were taken into account. Both theories agreed qualitatively with the experimental results concerning the temperature dependence of the polarization of the crystal.

In all works cited above, however, only the problem of giving a qualitative description of the sequence of PTs was solved. In the light of the fact that the *IC*-phase exists in only a very narrow temperature range (of the order of 1 K), the problem of giving a quantitative description of the PTs seems to us to be quite important. In this connection we had to extend Heine's model,[9] adding the interaction between the permanent dipoles of the NGs and the elastic dipoles. Second, the possibility of the existence in $NaNO_2$ of a riplon phase (R) between the *IC*-phase and the ferroelectric phase has not been examined. In addition, in this paper we shall construct the phase diagram in the temperature-pressure plane.

ORIENTATIONAL STATES

In the paraelectric phase the structure of $NaNO_2$ belongs to the body-centered orthorhombic group (space group D^{25}) with unit-cell dimensions $a = 3.725$ Å, $b = 5.73$ Å, and $c = 5.325$ Å at $t \approx 220$ °C.[12] The equilibrium positions of the atoms are determined by the vector $\mathbf{r}_{ni}$, where n designates the unit cell and i designates the type of atom in the unit cell: for NO_2 $i = 1$ and for Na $i = 2$. The nearest neighbors of the NGs consist of six Na^+ ions and ten NO_2^- ions (Fig. 2). This environment creates an orientational potential V for the NGs through the short-range repulsive interactions. It is well-known that it has two absolute minima in the directions $\pm\mathbf{b}$ and determines the preferred rotation axis, which is parallel to the line connecting the oxygen atoms and is directed along the c-axis.[3] In the calculations below we shall assume that this preferred axis is also the only rotation axis of the NG. In addition, we shall assume that the NG is absolutely rigid.

We determine the position of the center of rotation of the NG as the intersection of its rotation axis and the bisec-

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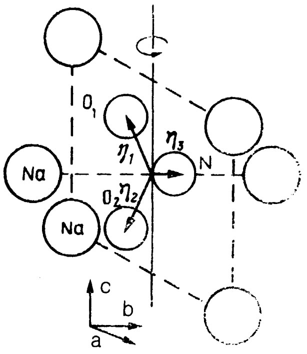

FIG. 1.

tor of the angle O–N–O. We orient the z coordinate axis along the rotation axis of the NG, we orient the x and y axes along the **a** and **b** axes, respectively, and we determine the relative coordinates of the O_1, O_2, and N atoms of the nitrite group in the nth unit cell (Fig. 1):

$$\begin{cases} \boldsymbol{\eta}_i = \mathbf{d}_i + \mathbf{z}_i, \quad i = 1, \ldots, 3, \\ \mathbf{d}_1 = -d_0 (\cos\varphi, \sin\varphi, 0), \quad \mathbf{d}_2 = -d_0 (\cos\varphi, \sin\varphi, 0), \\ \mathbf{d}_3 = d (\cos\varphi, \sin\varphi, 0), \\ \mathbf{z}_{1,2} = (0, 0, \pm z_0), \quad \mathbf{z}_3 = 0, \\ d_0 + d = l_0 \cos\alpha, \quad z_0 = l_0 \sin\alpha, \end{cases} \tag{1}$$

where $l_0 = 1.215$, $d_0 = 0.303$, $d = 0.365$ (in Å) and $\alpha = 113.2°$ (Ref. 13).

We describe the repulsive interactions between the atoms of the NG and the nearest neighbors by means of the Born–Mayer potential

$$U = C_1 \exp(-C_2 R), \tag{2}$$

where the Na–Na, N–N, and O–O interaction constants are taken, respectively, from Refs. 14–16 and are presented in Table I, while the mixed interaction constants are determined from the relations[17]

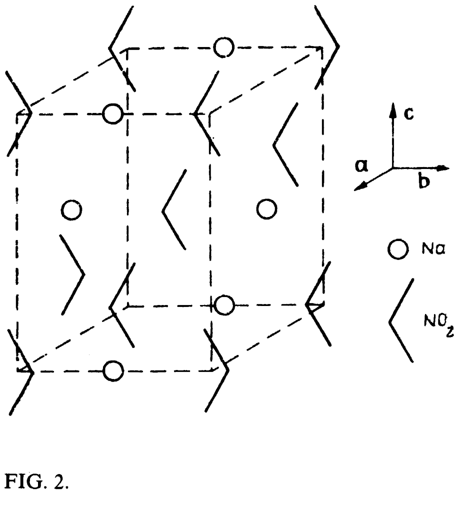

FIG. 2.

TABLE I.

Bonds	$C_1(i,i)$, ergs	$C_2(i,i)$, Å^{-1}
Na–Na	$0{,}21 \cdot 10^{-9}$	2,90
N–N	$3{,}41 \cdot 10^{-9}$	3,60
O–O	$5{,}40 \cdot 10^{-9}$	4,18

$$C_1(i,j) = [C_1(i,i) C_1(j,j)]^{1/2}, \quad C_2(i,j) = [C_2(i,i) + C_2(j,j)]/2,$$

where $i, j =$ Na, N, and O. Using the Born–Mayer interaction (2), we write the interaction of a NG with the Na atoms from the neighboring metal environment as[2,3]

$$U_1(\varphi) = \sum_{\mu} \sum_{s=1}^{3} C_1(\text{Na}, s) \exp[-C_2(\text{Na}, s) |\boldsymbol{\mu} - \boldsymbol{\eta}_s(\varphi)|] \tag{3}$$

and the interaction with the nearest NGs

$$U_2 = \sum_{1} \sum_{s,s'=1}^{3} C_1(s, s') \exp[-C_2(s, s') |\boldsymbol{\eta}_s(\varphi_1) - \boldsymbol{\eta}_{s'}(\varphi) + \mathbf{1}|], \tag{4}$$

where μ runs over the sixth nearest metal ions, 1 runs over the 10 nearest NGs, and s labels the atoms in a NG according to the formulas (1). The Coulomb energy, which is associated with the charges of the crystal and is related with the existence of the dipole moment of the NG $\mathbf{p}_n = p(\cos\varphi_n, \sin\varphi_n, 0)$, has the following form

$$W = W_{ep} + W_{pp},$$

where

$$W_{ep} = \sum_{\mathbf{n}, \mathbf{n}', i} e_{\mathbf{n}'i} [\mathbf{p}_{\mathbf{n}} (\mathbf{r}_{\mathbf{n}'i} - \mathbf{r}_{\mathbf{n}i})] / |\mathbf{r}_{\mathbf{n}'i} - \mathbf{r}_{\mathbf{n}i}|^3 \tag{5}$$

is the energy of interaction of the dipole moments of the NGs with the charges of the ions Na^+ and NO_2^-, and $\{e_{mi}\} = \{\pm e\}$,

Na^+, NO_2^- $\{e_{mi}\} = \{\pm e\}$,

$$W_{pp} = \frac{1}{2} \sum_{\mathbf{n}, \mathbf{n}'} \frac{(\mathbf{p}_{\mathbf{n}} \mathbf{p}_{\mathbf{n}'}) \mathbf{r}_{\mathbf{n}\mathbf{n}'}^2 - (\mathbf{p}_{\mathbf{n}} \mathbf{r}_{\mathbf{n}\mathbf{n}'}) (\mathbf{p}_{\mathbf{n}'} \mathbf{r}_{\mathbf{n}\mathbf{n}'})}{\mathbf{r}_{\mathbf{n}\mathbf{n}'}^5} \tag{6}$$

is the energy of the dipole-dipole interactions of NGs, and $\mathbf{r}_{\mathbf{nn}'} = \mathbf{r}_{\mathbf{n}1} - \mathbf{r}_{\mathbf{n}'1}$. One can see from Eqs. (3)–(6) that the force acting on an ion depends on the entire collection of values of $\{\varphi_n\}$, so that to each collection of angles there is associated its own collection of equilibrium positions $\{\mathbf{r}_{\mathbf{n}i}\}$. In order to transform to a lattice that does not depend on the positions of the NGs, we expand the expressions (3) and (4), which contain information about the form of the NGs, in powers of the small quantities d/μ, d_0/μ, d/l, and d_0/l. Now the angle-independent part of the potential energy of the crystal, which is the potential energy of the lattice, can be used to determine the equilibrium positions of the ions $\{\mathbf{r}_{ni}\}$. It is natural to assume that $\{\mathbf{r}_{ni}\}$ are also the average equilibrium positions of the crystal in the paraelectric phase. The angular part of the expansion of the expansions (3) and (4) consists of the crystal field, in which the NG rotates, and the two-particle NG–NG interactions. Correspondingly, we shall write out only their leading terms:

$$U(\varphi)=\sum_{\mu}\sum_{s=1}^{3}C_1(s,\mathrm{Na})\exp[-C_2(s,\mathrm{Na})(\mu^2+z_s^2)^{1/2}]$$
$$\times\frac{[C_2(s,\mathrm{Na})\boldsymbol{\mu}\mathbf{d}]^2}{\mu^2+z_s^2}$$
$$+\sum_{\mathbf{l}}\sum_{s,s'=1}^{3}C_1(s,s')\exp[-C_2(s,s')(l^2+z_s^2+z_{s'}^2)^{1/2}]$$
$$\times\frac{[C_2(s,s')\mathbf{l}\mathbf{d}_s]^2}{l^2+z_s^2+z_{s'}^2}. \qquad (7)$$

$$W(\varphi_n,\varphi_{n+l})=-\sum_{s,s'=1}^{3}C_1(s,s')\exp[-C_2(s,s')(l^2+z_s^2+z_{s'}^2)^{1/2}]$$
$$\times\frac{(\mathbf{d}_s(\mathbf{n})\mathbf{l})(\mathbf{d}_{s'}(\mathbf{n}+\mathbf{l})\mathbf{l})}{l^2+z_s^2+z_s'^2}, \qquad (8)$$

where

$$\begin{cases}\boldsymbol{\mu}_{1,2}=(0,\pm b,0), & \boldsymbol{\mu}_{3,\dots,6}=(\pm a,0,\pm c)/2,\\ \mathbf{l}_{1,\dots,8}=(\pm a,\pm b,\pm c)/2, & \mathbf{l}_{9,10}=\pm a/2.\end{cases} \qquad (9)$$

Generally speaking, the potential in which a NG rotates is determined by the sum of the expressions (5) and (7), but because of the symmetry of the crystal in the paraelectric phase the energy satisfies $W_{\mathrm{ep}}=0$. The crystal field, calculated taking into account the relations (1) and (9) and the leading term (7), has the form, to within an unimportant constant,

$$U(\varphi)=U_0(\cos 2\varphi+0{,}08\cos 4\varphi), \qquad (10)$$

where $U_0=1.3\cdot 10^{-13}$ ergs. The other harmonics are at most $6\cdot 10^{-3}$. The height of the potential barrier (10) $\Delta U\approx 2U_0=2.6\cdot 10^{-13}$ ergs, which is close to the experimentally observed value $3.1\cdot 10^{-13}$ ergs.[18]

The Hamiltonian of the NG will thus have the form of the Hamiltonian of a two-dimensional rotator:

$$H_R=-\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}+U(\varphi), \qquad (11)$$

where I is the moment of inertia of the NG relative to the z-axis and is equal to $7.82\cdot 10^{-40}$ g·cm². We present below five energy levels and the corresponding eigenfunctions of the operator (11), obtained by the Rayleigh–Ritz variational method:[19]

$$A_{1g}:\ E_1^0=-1{,}252,$$
$$\psi_1=(0{,}51-0{,}65\cos 2\varphi+0{,}47\cos 4\varphi-0{,}28\cos 6\varphi+0{,}14\cos 8\varphi-0{,}05\cos 10\varphi)/\pi^{1/2},$$
$$B_{2u}:\ E_2^0=-1{,}243,$$
$$\psi_2=(0{,}71\sin\varphi-0{,}57\sin 3\varphi+0{,}36\sin 5\varphi-0{,}16\sin 7\varphi)/\pi^{1/2},$$
$$B_{3u}:\ E_3^0=-0{,}981,$$
$$\psi_3=(-0{,}43\cos\varphi+0{,}62\cos 3\varphi-0{,}54\cos 5\varphi+0{,}34\cos 7\varphi-0{,}14\cos 9\varphi)/\pi^{1/2},$$
$$B_{1g}:\ E_4^0=-0{,}972,$$
$$\psi_4=(0{,}24\sin 2\varphi-0{,}58\sin 4\varphi+0{,}62\sin 6\varphi-0{,}44\sin 8\varphi)/\pi^{1/2},$$
$$A_{1g}:\ E_5^0=-0{,}697,$$
$$\psi_5=(0{,}39-0{,}28\cos 2\varphi-0{,}27\cos 4\varphi+0{,}59\cos 6\varphi-0{,}53\cos 8\varphi+0{,}26\cos 10\varphi)/\pi^{1/2}. \qquad (12)$$

Here A_{1g}, B_{1g}, B_{2u}, and B_{3u} designate the irreducible representations of the group D_{2h}[19] and the energy levels are measured in units of 10^{-13} ergs. Since the transition temperature $kT_c\approx 6.1\cdot 10^{-14}$ ergs, we can neglect the fifth energy level and confine our attention to the four-dimensional representation of the Hubbard operators,[1] constructed based on the eigenstates (12) $\hat{X}^{\alpha\beta}=|\alpha\rangle\langle\beta|$, which are matrices consisting of zeros, with the exception of the matrix element $\alpha\beta$, which is equal to unity. In particular, the Hamiltonian of the NG (11) in this representation has the form

$$H_R=\sum_{\mathbf{n}}E_\alpha^0\hat{X}_{\mathbf{n}}^{\alpha\alpha}. \qquad (13)$$

The two-particle NG–NG interactions assumes the form

$$W={}^1/_2\sum_{\mathbf{nn}'}\langle\alpha\gamma|W_{\mathbf{nn}'}|\delta\beta\rangle\,\hat{X}_{\mathbf{n}}^{\alpha\beta}\hat{X}_{\mathbf{n}'}^{\gamma\delta}, \qquad (14)$$

where

$$\langle\alpha\gamma|W_{\mathbf{nn}'}|\delta\beta\rangle=\int_0^{2\pi}\int_0^{2\pi}\psi_\alpha(\varphi_{\mathbf{n}})\psi_\beta(\varphi_{\mathbf{n}})W(\varphi_{\mathbf{n}},\varphi_{\mathbf{n}'})$$
$$\times\psi_\gamma(\varphi_{\mathbf{n}'})\psi_\delta(\varphi_{\mathbf{n}'})\,d\varphi_{\mathbf{n}}\,d\varphi_{\mathbf{n}'} \qquad (15)$$

are the matrix elements of the pair interactions.

$NaNO_2$ HAMILTONIAN

The total energy of the crystal consists of the interactions between the metal ions, between the metal ions and NG, and finally between the nitrite groups. In addition, aside from the rotational degrees of freedom of the NGs, represented by the Hamiltonian (11) and (13), it is, of course, also necessary to take into account the translational degrees of freedom of both the Na ions and the nitrite groups. Thus the Hamiltonian of the $NaNO_2$ crystal has the form

$$H=H_R+H_T+V+W, \qquad (16)$$

where H_T is the energy of the translational degrees of freedom and is determined by the electrostatic interactions and the short-range Born–Mayer interactions, V describes the coupling between the rotational degrees of freedom of the NG and its displacements, and W is the sum of all NG–NG pair interactions:

$$W=W_{pp}+{}^1/_2\sum_{\mathbf{n},l} W(\varphi_{\mathbf{n}},\varphi_{\mathbf{n}+l}). \qquad (17)$$

In order to simplify the notation we shall describe the translational degrees of freedom by the displacements directed along the **b** axis (i.e., along the y axis), since the spontaneous displacements of the NGs and Na atoms in the incommensurate and ferroelectric phases occur precisely along this axis.[20] Then in the harmonic approximation

$$H_T={}^1/_2\sum_{\mathbf{n}}\sum_{\mu} g(\mu)\,(u_{\mathbf{n}1}-u_{\mathbf{n}+\mu 2})^2, \qquad (18)$$

where $g(\mu_1)=g(\mu_2)=g_1$, $g(\mu_3)=\ldots=g(\mu_6)=g_2$ are, respectively, the force constants, which take into account the interactions of the NGs with the Na ions along the **b** axis and the plane orthogonal to this axis, and $u_{\mathbf{n}i}$ is the displacement of the ith atom in the **n**th unit cell. These force constants are related with the elastic moduli as follows:

$$g_1=2acC_{22}/b,\quad g_2=bcC_{66}/a.$$

Substituting the known values for $NaNO_2$, i.e., $C_{22}=3.8\cdot 10^{11}$ ergs/cm^3 and $C_{66}=0.5\cdot 10^{11}$ ergs/cm^3 (Ref. 21) and the dimensions of the unit cell,[12] we obtain

$$g_1=2{,}62\cdot 10^4 \text{ ergs/cm}^2,\quad g_2=0{,}42\cdot 10^4 \text{ ergs/cm}^2. \qquad (19)$$

In order to obtain the explicit form of the operator corresponding to the interaction of the rotational and translational degrees of freedom, we return to the expressions (3) and (5). Making in them the substitutions

$$\mathbf{r}_{\mathbf{n}i}\to\mathbf{r}_{\mathbf{n}i}+u_{\mathbf{n}i},\qquad \mu\to\mu+(u_{\mathbf{n}+\mu 2}-u_{\mathbf{n}1}) \qquad (20)$$

and making an expansion in the displacement $\mathbf{u}_{\mathbf{n}i}$, we obtain to a first approximation

$$V=\sum_{\mathbf{n}}\sum_{\mathbf{m}}\sum_{j} pe\sin\varphi_m V_j(\mathbf{n},\mathbf{m})\,(u_{\mathbf{n}j}-u_{\mathbf{m}1})$$

$$+\sum_{\mathbf{n}}\sum_{\mu} V_3(\mu,\mathbf{n})\,(u_{\mathbf{n}+\mu 2}-u_{\mathbf{n}1}), \qquad (21)$$

where

$$V_j(\mathbf{n},\mathbf{m})=\frac{1-3(\mathbf{r}_{\mathbf{n}j}-\mathbf{r}_{\mathbf{m}1})_y^2/(\mathbf{r}_{\mathbf{n}j}-\mathbf{r}_{\mathbf{m}1})^2}{|\mathbf{r}_{\mathbf{n}j}-\mathbf{r}_{\mathbf{m}1}|^3},\quad j=1,2, \qquad (22)$$

$$V_3(\mu,\mathbf{n})=-\sum_s C_1(\text{Na},s)C_2(\text{Na},s)$$

$$\times\exp[-C_2(\text{Na},s)|\mu-\mathbf{z}_s|]\frac{(\mu-\mathbf{d}_s(\varphi))_y}{|\mu-\eta_s|}. \qquad (23)$$

Next, substituting into Eq. (21) the values of the dipole moment of the NG $p=0.372$ D and the charge $e=4.8\cdot 10^{-10}$ CGS units and projecting this interaction on the characteristic four-dimensional representation of the NG, described by the functions (12), we obtain

$$V=\sum_{\mathbf{n}} V_{\alpha\beta}(\mathbf{n})\hat{X}_{\mathbf{n}}^{\alpha\beta}=\sum_{\mathbf{n}}\Big[\Delta_1(\mathbf{n})\Lambda_1^{\alpha\beta}(\mathbf{n})+\Delta_2(\mathbf{n})\Lambda_2^{\alpha\beta}(\mathbf{n})$$

$$+\sum_{\mathbf{m}}\sum_{j}\lambda_{\alpha\beta}V_j(\mathbf{n},\mathbf{m})\,(u_{\mathbf{n}j}-u_{\mathbf{m}1})\Big]\hat{X}_{\mathbf{n}}^{\alpha\beta}, \qquad (24)$$

where $V_j(\mathbf{n},\ \mathbf{m})(j=1,\ 2)$ are dimensionless, and the coupling constants in units of 10^{-5} ergs/cm are equal to

$$\Lambda_1^{\alpha\beta}(\mathbf{n})=\langle\alpha|V_3(\mu_1,\mathbf{n})|\beta\rangle=-\begin{bmatrix}0 & 1{,}18 & 0 & 0\\ 1{,}18 & 0 & 0 & 0\\ 0 & 0 & 0 & 1{,}14\\ 0 & 0 & 1{,}14 & 0\end{bmatrix},$$

$$(25)$$

$$\Lambda_2^{\alpha\beta}(\mathbf{n})=\langle\alpha|V_3(\mu_3,\mathbf{n})|\beta\rangle=-\begin{bmatrix}0 & 0{,}57 & 0 & 0{,}07\\ 0{,}57 & 0 & 0{,}06 & 0\\ 0 & 0{,}06 & 0 & 0{,}55\\ 0{,}07 & 0 & 0{,}55 & 0\end{bmatrix},$$

$$\lambda_{\alpha\beta}=\begin{bmatrix}0 & 17{,}7 & 0 & 0\\ 17{,}7 & 0 & 0 & 0\\ 0 & 0 & 0 & 17{,}3\\ 0 & 0 & 17{,}3 & 0\end{bmatrix},$$

and the combinations of displacements

$$\Delta^1(\mathbf{n})=u_{\mathbf{n}+\mu_1 2}+u_{\mathbf{n}+\mu_2 2}-2u_{\mathbf{n}1},\qquad \Delta^2(\mathbf{n})=\sum_{i=3}^{6}(u_{\mathbf{n}+\mu_i 2}-u_{\mathbf{n}1}).$$

$$(26)$$

The pair interactions (17), taking into account Eqs. (4), (6), (14), and (15), have the form

$$W=\sum_{\mathbf{n},\mathbf{n}'} W_{\mathbf{n}\mathbf{n}'}\hat{Y}_{\mathbf{n}}\hat{Y}_{\mathbf{n}'}, \qquad (27)$$

where

$$\hat{Y}=\hat{X}^{12}+\hat{X}^{34}+\text{h.c.},$$

$$W_{\mathbf{n}\mathbf{n}'}=W_{\mathbf{n}\mathbf{n}'}^{1212}=W_pV_1(\mathbf{n},\mathbf{n}')+W_\eta\delta_{\mathbf{n}',\mathbf{n}+1},$$

$$W_p=|\langle 1|p_y|2\rangle|^2,\quad W_\eta=\langle 12|W(\varphi_{\mathbf{n}},\varphi_{\mathbf{n}+l})|21\rangle,$$
$$\langle 1|p_y|2\rangle=0{,}96p,\quad \langle 12|W(\varphi_{\mathbf{n}},\varphi_{\mathbf{n}+l})21\rangle=-2{,}3\cdot 10^{-16}\text{ ergs}.$$

$$(28)$$

Here we have employed the fact that with the exception of the matrix elements

$$|\langle 1|p_y|2\rangle|\approx|\langle 3|p_y|4\rangle|,$$

$$\langle 12|W(\varphi_{\mathbf{n}},\ \varphi_{\mathbf{n}+l})|21\rangle\approx\langle 34|W(\varphi_{\mathbf{n}},\ \varphi_{\mathbf{n}+l})|43\rangle,$$

the other matrix elements are equal to zero or are small.

FREE ENERGY

We analyze the structural transformations in the $NaNO_2$ crystal on the basis of the effective free energy, written in terms of the translational degrees of freedom $u_{\mathbf{n}i}$ (Ref. 1)

$$F(u)=H_T-kT\ln \mathrm{Sp}\{\exp[-\beta(H_R+V+W)]\}, \qquad (29)$$

where Sp denotes summation over all four states of each NG. In order to carry out this summation, we write the pair interactions in the molecular-field approximation

$$\hat{W}=\sum_{\mathbf{n},\mathbf{n}'} W_{\mathbf{n}\mathbf{n}'}\hat{Y}_{\mathbf{n}}\langle\hat{Y}_{\mathbf{n}'}\rangle. \qquad (30)$$

Then the self-consistency equations will assume the form

$$Y_{\mathbf{n}}=\langle\hat{Y}_{\mathbf{n}}\rangle=\frac{\mathrm{Sp}\{\hat{Y}_{\mathbf{n}}\exp[-\beta(H_R+V+\hat{W})]\}}{\mathrm{Sp}\{\exp[-\beta(H_R+V+\hat{W})]\}}. \qquad (31)$$

In order to carry out the Sp operation in Eq. (26) it is necessary to diagonalize the matrix

$$H_R+V+\hat{W}=\sum_n\begin{bmatrix} A(\mathbf{n}) & C(\mathbf{n}) \\ C(\mathbf{n}) & B(\mathbf{n})\end{bmatrix}, \qquad (32)$$

where

$$A(\mathbf{n})=\begin{bmatrix} E_1{}^0+V_{11}(\mathbf{n}) & V_{12}(\mathbf{n})+W(\mathbf{n}) \\ V_{21}(\mathbf{n})+W(\mathbf{n}) & E_2{}^0+V_{22}(\mathbf{n})\end{bmatrix},$$

$$B(\mathbf{n})=\begin{bmatrix} E_3{}^0+V_{33}(\mathbf{n}) & V_{34}(\mathbf{n})+W(\mathbf{n}) \\ V_{43}(\mathbf{n})+W(\mathbf{n}) & E_4{}^0+V_{44}(\mathbf{n})\end{bmatrix}, \qquad (33)$$

$$C(\mathbf{n})=\begin{bmatrix} 0 & V_{14}(\mathbf{n}) \\ V_{23}(\mathbf{n}) & 0\end{bmatrix},$$

$$W(\mathbf{n})=\sum_{\mathbf{n}} W_{\mathbf{n}\mathbf{n}'}\langle\hat{Y}_{\mathbf{n}'}\rangle.$$

The ratio of the energies (12) and the coupling constants (25) is such that the eigenvalues of the matrix

$$\begin{bmatrix} A(\mathbf{n}) & 0 \\ 0 & B(\mathbf{n})\end{bmatrix} \qquad (35)$$

are equal to the eigenvalues of the matrix (32) to within $(\Lambda_2^{14}/\Lambda_2^{12})^2\sim 10^{-2}$. For this reason, in what follows we approximate the Hamiltonian (32) by the matrix (35), whose eigenvalues are equal to

$$E_{1,2}=(A_{11}+A_{22})/2\mp\{[(A_{11}-A_{22})/2]^2+A_{12}{}^2\}^{1/2}=-\varepsilon_1\mp\vartheta_1,$$

$$E_{3,4}=(B_{11}+B_{22})/2\mp\{[(B_{11}-B_{22})/2]^2+B_{12}{}^2\}^{1/2}=-\varepsilon_2\mp\vartheta_2. \qquad (36)$$

On the basis of the relations (24) and (32), we have

$$\langle X_{\mathbf{n}}{}^{12}\rangle=-\frac{1}{\beta}\frac{\delta\ln Z(\mathbf{n})}{\delta A_{12}(\mathbf{n})}, \qquad \langle X_n{}^{34}\rangle=-\frac{1}{\beta}\frac{\delta\ln Z(\mathbf{n})}{\delta B_{12}(\mathbf{n})},$$

where

$$Z(\mathbf{n})=2\exp(\beta\varepsilon_1)\,\mathrm{ch}\,\beta\vartheta_1+2\exp(\beta\varepsilon_2)\,\mathrm{ch}\,\beta\vartheta_2,$$

whence we obtain

$$Y_{\mathbf{n}}=-\frac{A_{12}\vartheta_1{}^{-1}\exp(\beta\varepsilon_1)\,\mathrm{sh}\,\beta\vartheta_1+B_{12}\vartheta_2{}^{-1}\exp(\beta\varepsilon_2)\,\mathrm{sh}\,\beta\vartheta_2}{\exp(\beta\varepsilon_1)\,\mathrm{ch}\,\beta\vartheta_1+\exp(\beta\varepsilon_2)\,\mathrm{ch}\,\beta\vartheta_2}. \qquad (37)$$

This equation is the self-consistency equation, since, as one can see from the relations (36), (33), and (34), the matrix elements contain the averages $Y_{\mathbf{n}}$.

In order to expand the thermodynamic potential (29) in a series in the displacements, we make some estimates. From the expressions (24), (25), (33), and (36) it follows that

$$A_{11}-A_{22}=-\omega_0\approx-10^{-15}\text{ ergs},\quad B_{11}-B_{22}\approx-\omega_0,$$

$$\varepsilon_1\approx 1{,}25\cdot 10^{-13}\text{ ergs},\quad \varepsilon_2\approx-0{,}977\cdot 10^{-13}\text{ ergs}.$$

Next, it is obvious from the formulas (25) and (33) that $A_{12}\approx B_{12}$. As a result, near a PT, where the displacements are small, so that

$$\beta\vartheta_1\ll 1,\quad \beta\vartheta_2\ll 1,$$

the self-consistency equations (37) can be replaced by the linearized equation

$$Y_{\mathbf{n}}=-\beta A_{12}=-\beta\Big[\Delta_1(\mathbf{n})\Lambda_1{}^{12}(\mathbf{n})+\Delta_2(\mathbf{n})\Lambda_2{}^{12}(\mathbf{n}) + \sum_{\mathbf{m}}\sum_j \lambda_{12}V_j(\mathbf{n},\mathbf{m})(u_{\mathbf{n}j}-u_{\mathbf{m}1})\Big]-\beta\sum_{\mathbf{n}'}W_{\mathbf{n}\mathbf{n}'}Y_{\mathbf{n}'}, \qquad (38)$$

which relates the spontaneous deformations with the ordering parameter of the NG.

The last expression in the thermodynamic potential (29), according to Eq. (36), equal to

$$\ln[\exp(\beta\varepsilon_1)\,\mathrm{ch}\,\beta\vartheta_1+\exp(\beta\varepsilon_2)\,\mathrm{ch}\,\beta\vartheta_2],$$

can be expanded in a series in the displacements, which gives

$$F(u)=H_T-{}^1/_2\sum_{\mathbf{n}}[\beta A_{12}{}^2(u_{\mathbf{n}i},Y_{\mathbf{n}})-{}^1/_6\beta^3A_{12}{}^4(u_{\mathbf{n}i},Y_{\mathbf{n}})]. \qquad (39)$$

Here we have employed the fact that $\beta\omega_0\ll 1$. Since the averages $Y_{\mathbf{n}}$ can be expressed in terms of $u_{\mathbf{n}i}$ with the help of the self-consistency equations (38), we can see that the expression (39) is the thermodynamic potential of the translational degrees of freedom $u_{\mathbf{n}i}$.

Fourier transforming,

$$u_{\mathbf{n}j}=N^{-1/2}\sum_{\mathbf{k}}u_{\mathbf{k}j}\exp(i\mathbf{kn}),\qquad Y_n=N^{-1/2}\sum_{\mathbf{k}}Y_k\exp(i\mathbf{kn}),$$

$$V_j(\mathbf{n},\mathbf{m})=V_j(\mathbf{n}-\mathbf{m})=N^{-1/2}\sum_k V_j(\mathbf{k})\exp[ik(\mathbf{n}-\mathbf{m})], \qquad (40)$$

we obtain instead of Eq. (38)

$$Y_{\mathbf{k}}=\beta[h_1(\mathbf{k})u_{\mathbf{k}1}-h_2(\mathbf{k})u_{\mathbf{k}2}]/[1+\beta W(\mathbf{k})], \qquad (41)$$

where

$$h_1(\mathbf{k})=2(\Lambda_1{}^{12}+2\Lambda_2{}^{12})+[V_1(\mathbf{k})-V_1(\mathbf{k}=0)+V_2(\mathbf{k}=0)]\lambda_{12},$$

$$h_2(\mathbf{k})=2[\Lambda_1{}^{12}\cos(\mathbf{kb}/2)+2\Lambda_2{}^{12}\cos(\mathbf{ka}/2)\cos(\mathbf{kc}/2)]\times\exp(-i\mathbf{kb}/2)+\lambda_{12}V_2(\mathbf{k}),$$

$$W(\mathbf{k})=W_pV_1(\mathbf{k})+2W_\eta[\cos(\mathbf{ka})+4\cos(\mathbf{ka}/2)\cos(\mathbf{kb}/2)\cos(\mathbf{kc}/2)]. \qquad (43)$$

It is easy to show, using the invariance of Eq. (22) under an interchange of the arguments

$$V_j(\mathbf{n},\mathbf{m})=V_j(\mathbf{m},\mathbf{n}),$$

that $V_j(\mathbf{k})$ are real functions. Numerical analysis shows that, in agreement with the experimental data of Ref. 22, the potential $V_1(\mathbf{k})$ has a minimum which is typical for the existence of the *IC*-phase, for a wave vector inside the Brillouin zone and directed along the *a* axis (Fig. 3), while the potential $V_2(\mathbf{k})$ has a minimum at the edge of the zone[23] for $\mathbf{k}=(2\pi/a, 0, 0)$. In what follows we shall assume that the wave vector has a component only along the **a** axis: $\mathbf{k}=(\xi a^*, 0, 0)$.

Transforming to **k**-space and substituting for Y_k the expression (41), we obtain the thermodynamic potential in the variables u_{ki}:

$$F={}^1/_2\sum_k\sum_{i,j=1}^{2}D_{ij}(k)\,u_{ki}u_{kj}^*$$
$$+{}^1/_4\sum_{\{k_l\}}\sum_{jmnl}b(k_1,k_2,k_3,k_4)\,\delta(k_1+k_2+k_3+k_4)\,u_{k_1j}u_{k_2m}u_{k_3n}u_{k_4l}, \qquad (44)$$

where

$$D_{11}(k)=2(g_1+2g_2)-\beta h_1^2(k)/[1+\beta W(k)]^2,$$
$$D_{22}(k)=2(g_1+2g_2)-\beta h_2^2(k)/[1+\beta W(k)]^2,$$
$$D_{12}(k)=D_{21}(k)=-2(g_1+2g_2\cos(ka/2))$$
$$+\beta h_1(k)h_2(k)/[1+\beta W(k)]^2. \qquad (45)$$

We do not present the expression for the positive-definite coupling constant $b(k_1, k_2, k_3, k_4)$, since it is not employed in this work.

PHASE DIAGRAM

In order to analyze the thermodynamic potential (44) we diagonalize the matrix (45) in it, after which we obtain

$$F={}^1/_2\sum_k[\Omega_1^2(k)Q_{k1}^2+\Omega_2^2(k)Q_{k2}^2]$$
$$+{}^1/_4\sum_{\{k_l\}}\sum_{jmnl}\tilde{b}(k_1,k_2,k_3,k_4)\,\delta(k_1+k_2+k_3+k_4)\,Q_{k_1j}Q_{k_2m}Q_{k_3n}Q_{k_3l}, \qquad (46)$$

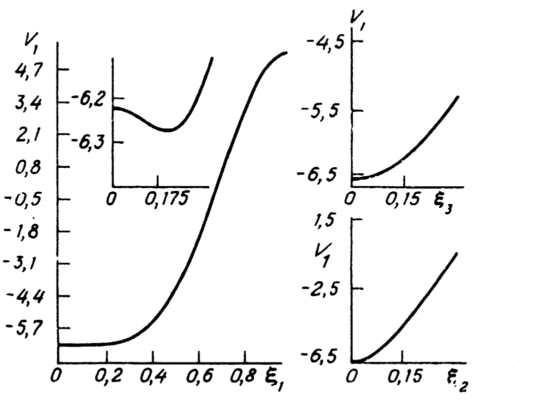

FIG. 3. Graphs of $V_1(k)$ in units of 10^{-2} Å^{-3} for $k=\xi_1a^*$, $k=a^*/4+\xi_2b^*$, and $k=a^*/4+\xi_3c^*$.

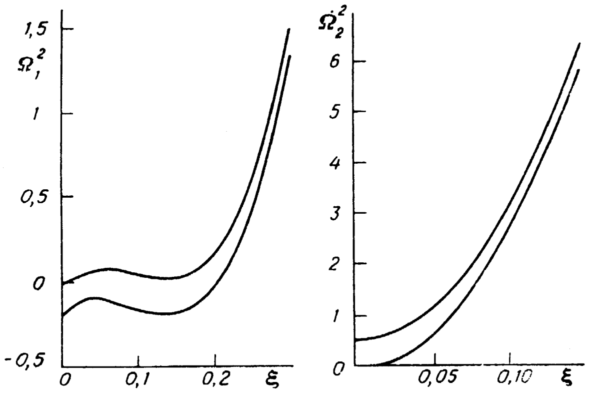

FIG. 4. Behavior of Ω_1^2 and Ω_2^2 at $T=T_i$ (upper curves) and $T\leqslant T_c$ (lower curves).

where

$$\Omega_{1,2}^2(k)=(D_{11}+D_{22})/2\mp\{[(D_{11}-D_{22})/2]^2+D_{12}^2\}^{1/2} \qquad (47)$$

are the squared effective frequencies of, respectively, the acoustic and optical modes, which, in reality, represent the inverse susceptibilities of the normal coordinates Q_{ki}. The displacements u_{ki} are related to the normal coordinates Q_{ki} by the transformation

$$\begin{bmatrix}u_{k1}\\u_{k2}\end{bmatrix}=[[D_{22}-\Omega_1^2]^2+D_{12}^2]^{-1/2}$$
$$\times\begin{bmatrix}D_{22}(k)-\Omega_1^2(k) & D_{12}(k)\\-D_{12}(k) & D_{22}(k)-\Omega_1^2(k)\end{bmatrix}\begin{bmatrix}Q_{k1}\\Q_{k2}\end{bmatrix}. \qquad (48)$$

The temperature dependence of the frequencies (47) is presented in Fig. 4 and has the following features. First, as the temperature decreases there arises on the lower branch a minimum at a value of **k** different from zero, which vanishes at the point $\mathbf{k}_i=\xi_i\mathbf{a}^*$, where $\xi_i\approx 0.134$ at the critical temperature $T_i\approx 442$ K. Figure 5 shows the numerical analysis for T_i and the reduced wave vector ξ_i as a function of the

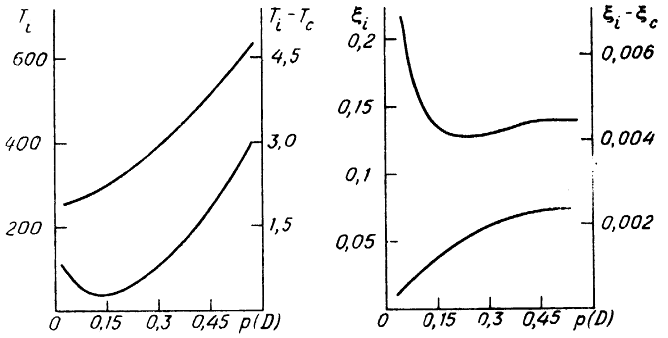

FIG. 5. The temperature of the transition into the IC-phase (upper curve) and the temperature interval in which this phase exists (lower curve) as functions of the dipole moment. The reduced wave vector ξ_i (upper curve) and the difference $\xi_i-\xi_c$ (lower curve) a function of the dipole moment.

magnitude of the dipole moment p of the NG. This dependence is of interest because when the ionic crystal is doped[24] the dipole moment of the NG changes in the range $0.2D$–$0.97D$ and the dependence presented makes it possible to judge, on the basis of the transition temperature, the dipole moment of NG in $NaNO_2$. Returning to this feature, with regard to the temperature dependence of $\Omega_1^2(k)$ it should be noted that it leads to a PT into the incommensurate or modulated phase, where the spatial dependence of the displacements is determined by the formula (48) with the corresponding substitution for $\Omega_1(k_i)$ and $Q_{k2} = 0$.

Second, from the formulas (43), (45), and (47) we obtain

$$\Omega_{1,2}^2(0) = D_{11} \mp |D_{11}|. \tag{49}$$

As the temperature decreases the quantity D_{11} vanishes at the temperature

$$T_0 = \frac{h_1^2(0)}{4(g_1+2g_2)} - W(0) + \left[\frac{h_1^4(0)}{16(g_1+2g_2)^2} - \frac{h_1^2(0)W(0)}{2(g_1+2g_2)}\right]^{1/2} \tag{50}$$

and then becomes negative. In addition, it follows from the formula (49) that for $T < T_0$ $\Omega_2^2(0)$ remains equal to zero while $\Omega_1^2(0)$ becomes negative, as shown in Fig. 4, and therefore the mode Q_{k1} is unstable at $k = 0$. Thus if fluctuations of the order parameter are ignored, two normal modes can be retained in Eq. (46): $Q_i = Q_1(k_i)$ and $Q_0 = Q_1(k = 0)$, and the thermodynamic potential of the two interacting single-component order parameters can be written as[25]

$$F = \tau_i Q_i^2 + {}^1/_2 \tau_0 Q_0^2 + {}^1/_4 \gamma Q_0^4 + {}^3/_2 \delta Q_i^4 + 3\eta Q_0^2 Q_i^2, \tag{51}$$

where

$$\tau_i = \Omega_1^2(k_i), \quad \tau_0 = \Omega_1^2(k=0),$$
$$\gamma = \tilde{\text{б}}(0, 0, 0, 0), \quad \delta = \tilde{\text{б}}(k, k, -k, -k), \quad \eta = \tilde{\text{б}}(0, 0, k, -k). \tag{52}$$

The equation of state

$$\begin{aligned} &(\tau_i + 3\delta Q_i^2 + 3\eta Q_0^2) Q_i = 0, \\ &(\tau_0 + \gamma Q_0^2 + 6\eta Q_i^2) Q_0 = 0, \end{aligned} \tag{53}$$

has three types of solutions, which we give below together with the corresponding thermodynamic potentials:

$$\begin{aligned} &1.\ Q_i^2 = -\tau_i/3\delta, \quad Q_0 = 0, \quad F_1(T, k) = -{}^1/_6 \tau_i^2/\delta; \\ &2.\ Q_0^2 = -\tau_0/\gamma, \quad Q_i = 0, \quad F_2(T, k=0) = -{}^1/_4 \tau_0^2/\gamma; \\ &3.\ Q_i^2 = {}^1/_3 \frac{3\eta\tau_0 - \gamma\tau_i}{\gamma\delta - \eta^2}, \quad Q_0^2 = \frac{2\eta\tau_i - \delta\tau_0}{\gamma\delta - \eta^2}, \\ &F_3(T) = [\tau_i\tau_0\eta - {}^1/_6 \gamma\tau_i - {}^1/_6 \delta\tau_i]/[\gamma\delta - 6\eta^2]. \end{aligned} \tag{54}$$

These phases are, respectively, the incommensurate, ferroelectric, and ripplon phases.[11] The regions of stability of the phases are determined from the inequalities[26]

$$F_{Q_iQ_i} \geqslant 0, \quad \begin{vmatrix} F_{Q_iQ_i} & F_{Q_iQ_0} \\ F_{Q_iQ_0} & F_{Q_0Q_0} \end{vmatrix} \geqslant 0 \tag{55}$$

and, together with the conditions of existence of the solutions (54)

$$\begin{aligned} &1.\ \tau_i \leqslant 0, \quad \delta > 0, \quad 2.\ \tau_0 \leqslant 0, \quad \gamma > 0, \\ &3.\ 3\eta\tau_0 - \gamma\tau_i > 0, \quad 2\eta\tau_i - \delta\tau_0 > 0, \quad \gamma\delta - 6\eta^2 > 0 \end{aligned}$$

have the form

$$\begin{aligned} &1.\ \tau_i \leqslant 0, \quad 2\eta\tau_i - \delta\tau_0 < 0; \\ &2.\ \tau_0 \leqslant 0, \quad 3\eta\tau_0 - \gamma\tau_i < 0; \\ &3.\ \gamma\delta - 6\eta^2 > 0, \quad 3\eta\tau_0 - \gamma\tau_i > 0, \quad 2\eta\tau_i - \delta\tau_0 > 0. \end{aligned} \tag{56}$$

Since the wave vector k_i lies close to the center of the Brillouin zone, we neglect the k-dependence in the coupling constants (52), i.e., we employ the approximation

$$\gamma = \delta = \eta. \tag{57}$$

In this case, according to the inequalities (56) only the solutions 1 and 2 of the solutions (54) are realized and the equations for determining the temperatures and the reduced wave vectors of the phase transitions

$$\begin{aligned} &F_1(T_i, k_i) = 0, \quad d\tau_i(k_i)/dk = 0, \\ &F_1(T_c, k_c) = F_2(T_c, 0), \quad d\tau_i(k_c)/dk = 0 \end{aligned} \tag{58}$$

have the form

$$\begin{aligned} &\tau_i = 0, \quad d\tau_i(k_i)/dk = 0, \\ &\tau_i^2 = {}^3/_2 \tau_0^2, \quad d\tau_i(k_c)/dk = 0. \end{aligned} \tag{59}$$

The solution of the first pair of equations in Eq. (59) gives the temperature of the PT into the IC-phase and the reduced vector of the IC-phase, while the solution of the second pair gives the temperature of the PT into the ferroelectric phase. The results of these solutions are presented in Fig. 5 as a function of the dipole moment of the NG.

Substituting the expressions for Q_i and Q_0 (54) into Eq. (48), we find the displacement of the ions in, respectively, the incommensurate phase

$$\begin{aligned} u_{n1} &= \frac{2[D_{22}(\mathbf{k}) - \Omega_1^2(\mathbf{k})] Q_i \cos(\mathbf{kn})}{\{[D_{22}(\mathbf{k}) - \Omega_1^2(\mathbf{k})]^2 + D_{12}^2(\mathbf{k})\}^{1/2}}, \\ u_{n2} &= \frac{-2D_{12}(\mathbf{k}) Q_i \cos(\mathbf{kn})}{\{[D_{22}(\mathbf{k}) - \Omega_1^2(\mathbf{k})]^2 + D_{12}^2(\mathbf{k})\}^{1/2}} \end{aligned} \tag{60}$$

and the ferroelectric phase

$$u_{n1} = Q_0/2^{1/2}, \quad u_{n2} = -Q_0/2^{1/2}. \tag{61}$$

The relation between the displacements of the ions in a unit cell and the position of the NG can be determined with the help of Eqs. (54), (48), and (41): as the ions move closer to one another the nitrogen ion of the NG moves to the position farthest away from the metal atom.

The sequence of phase transitions (58), which is obtained under the assumption (57), is identical to the sequence given in Refs. 5 and 22. In Ref. 10, however, in an analysis of the x-ray structural data it was concluded that between the phases I and II in an interval ≈ 0.2 K there exists a third phase III—the sinusoidal ferroelectric phase (ripplon phase). In our case the ripplon phase is described by the solution 3 in Eq. (54). Indeed, substituting this solution into Eqs. (48) and (50), we obtain the ion displacements corresponding to the sinusoidal ferroelectric phase

$$u_{\mathbf{n}1}=\frac{2[D_{22}(\mathbf{k})-\Omega_1^2(\mathbf{k})]Q_i\cos(\mathbf{kn})}{\{[D_{22}(\mathbf{k})-\Omega_1^2(\mathbf{k})]^2+D_{12}^2(\mathbf{k})\}^{1/2}}+Q_0 2^{-1/2},$$
$$u_{\mathbf{n}2}=\frac{-2D_{12}(\mathbf{k})Q_i\cos(\mathbf{kn})}{\{[D_{22}(\mathbf{k})-\Omega_1^2(\mathbf{k})]^2+D_{12}^2(\mathbf{k})\}^{1/2}}-Q_0 2^{-1/2}. \qquad (62)$$

The necessary condition for the existence of the solution 3 in Eq. (54) is the inequality

$$\gamma\delta-6\eta^2>0, \qquad (63)$$

which, on the basis of the relations (57), cannot, of course, be satisfied. However this relation can change significantly, if the anharmonic contributions to the translational part of the elastic energy of the crystal (18) are taken into account.

It is interesting to study the dependence of the temperature of the phase transition not only on the dipole moment p of the NG but also on the unit-cell parameters. This makes it possible to find the complete phase diagram of $NaNO_2$ in the temperature-pressure plane, since application of pressure gives rise to uniform lattice deformations

$$\begin{aligned}P_x&=C_{11}u_{xx}+C_{12}u_{xy}+C_{13}u_{xz},\\ P_y&=C_{21}u_{yx}+C_{22}u_{yy}+C_{23}u_{yz},\\ P_z&=C_{31}u_{zx}+C_{32}u_{zy}+C_{33}u_{zz},\end{aligned} \qquad (64)$$

which in turn change the unit-cell parameters

$$a\to a(1+u_{xx}),\quad b\to b(1+u_{yy}),\quad c\to c(1+u_{zz}), \qquad (65)$$

where $C_{11}=22$, $C_{22}=38$, $C_{33}=40$, $C_{12}=8.4$, $C_{13}=7.1$, $C_{23}=6.2$ in units of 10^{10} dynes/cm^2 (Ref. 21).

Since the effect of hydrostatic pressure ($P=P_x=P_y=P_c$) in $NaNO_2$ has been investigated experimentally,[27] we shall examine this case. Expressing in terms of P with the help of the formulas (64) and (65) the changes of the parameters of the unit cell, we calculate the transition temperature and the corresponding reduced wave vector using Eq. (59). The results of the calculations are presented in Fig. 6. For $P=10$ kbar the computed transition temperature T_i is 120 K higher than the experimental value, while the temperature window $T_i-T_c=8$K agrees with the experimental window. There are still no experimental data on the dependences $k_i=k_i(P)$ and $k_c=k_c(P)$.

CONCLUSIONS

The quite good agreement between the computed values $T_i=442.0$ K, $\xi_i=0.134$, $T_c=441.5$ K, and $\xi_c=0.132$ with $p=0.372D$ and the experimental data $T_i=437.0$ K, $\xi_i=0.12$, $T_c=435.7$ K, and $\xi_c=0.1$ with $p=0.41D$ (Refs. 28 and 29) indicates that the present model is adequate for describing the sequence of phase transitions in $NaNO_2$. However, the temperature dependence of the incommensurateness factor obtained in this work (Fig. 6) is an order of magnitude weaker than the dependence observed experimentally.[20] One way to obtain a strong temperature dependence of ξ_i is to take into account the fluctuations of the order parameters. However this would have made this account too long, so that it will be done in a separate paper.

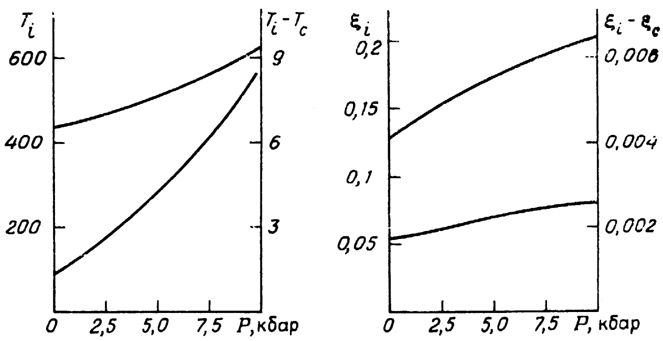

FIG. 6. The pressure dependences of the temperature of the transition into the IC-phase (upper curve) and the temperature interval in which this phase exists (lower curve). The pressure dependences of the reduced wave vector ξ_i (upper curve) and the difference ξ_i-i_c (lower curve).

It was found that the introduction of the interaction of elastic dipoles with NG, which are described by the first term in Eq. (21), was critical not only for the quantitative but also the qualitative behavior of the model. This interaction was found to be of the same order of magnitude as the Born–Mayer interaction (23), to say nothing of the importance of the form of the dependence $V_j(k)$, $j=1, 2$ (Fig. 3).

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