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Microscopic theory of lattice instability and incommensurate phase transition in $NaNO_2$

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The incommensurate (IC) phase transition in $NaNO_2$ is studied on the basis of a lattice dynamical model. At finite wave vector, molecular reorientations of the NO_2 groups around the crystallographic $\vec{c}$ axis are coupled to acoustic lattice displacements. A modulation, along the $\vec{a}$ axis, of nonequilibrium expectation values of the orientational order produces a modulation of expectation values of acoustic displacements with polarization in the $\vec{b}$ direction. The IC transition corresponds to a freezing-in of both types of motion. Connection with phenomenological theories is made. The temperature and wave-number behavior of diffuse x-ray scattering peaks above the IC transition is explained.

I. INTRODUCTION

Since the discovery of ferroelectricity in $NaNO_2$ by Sawada *et al.*,[1] this substance has attracted much attention as a model system for an order-disorder structural phase transition.[2] Generally, order-disorder transitions have been given this appellation in contradistinction to displacive transitions. The main experimental feature characterizing a displacive transition is the occurrence of a soft phonon at certain symmetry points in the Brillouin zone.[3] Such a phonon softening is absent in $NaNO_2$ as is shown from neutron scattering[4] and ultrasonic results.[5] Critical dynamics attributed to the reorientational motion of the NO_2 molecular groups has been investigated by neutrons[4] and by dielectric measurements.[6]

A very interesting fact in $NaNO_2$ is the occurrence of an incommensurate antiferroelectric phase[7] in a narrow temperature range between the paraelectric and the ferroelectric phases. This antiferroelectric phase was described as a sinusoidal modulation of the magnitude of the dipolar moments.[8,9] More recently, additional insight has been gained from x-ray[10,11] and neutron-diffraction[12] studies. The authors of Ref. 10 propose a model where in addition to the order-parameter modulation,[8,9] all atoms in the successive unit cells along the $\vec{a}$ axis are assumed to be sinusoidally displaced from their average positions in $\vec{b}$ direction. In Ref. 11, a theoretical interpretation of structure data led to a model where occupation factors of both equilibrium positions for the Na ion and the NO_2 molecule are modulated by a sine function. Finally the neutron results of Ref. 12 are interpreted in terms of a model which takes into account the modulation of the occupation probability of each atom. This leads to a long-range order parameter defined in successive sheets composed of the whole $\vec{b}\vec{c}$ plane and modulated along the $\vec{a}$ axis.

The previous results[10–12] suggest that the picture of an order-disorder transition applied to $NaNO_2$ so far is incomplete. Another indication in that direction of thought is obtained from an atomistic model of $NaNO_2$ which was proposed by Ehrhardt and the present author.[13] Based on the steric hindrance potential of the NO_2 molecule in the deformable cage of neighboring Na ions, the model leads to a Hamiltonian with bilinear coupling between translations and rotations. The latter are formulated in terms of symmetry-adapted functions. The orientational order parameter belongs to the ungerade representation B_u of the orthorhombic group. In the long-wavelength limit it couples only to optical lattice displacements. The model of Ref. 13 explains the absence of acoustic soft modes in the long-wavelength limit.[4] It also accounts for the temperature behavior of the elastic constants.[5] If one wants to extend the model to a description of the incommensurate (IC) phase transition, one has to study the properties of the bilinear coupling at finite wave vector.

From symmetry reasons it becomes obvious that away from the Brillouin-zone center there should exist a nonzero coupling between the orientational order parameter and acoustic displacements. This coupling should manifest itself at an incommensurate wave number and influence the nature of the modulated IC phase.

A phenomenological theory of the IC transition in $NaNO_2$ and $SC(NH_2)_2$ has been proposed by Levanyuk and Sannikov.[14] The authors consider the situation where a one-component order parameter η couples with a generalized coordinate ξ which has transformation properties different from η. Although a Lifshitz invariant[15,16] is absent in the case of a one-component order parameter, the existence of gradient invariants of type $\eta\delta\xi/\delta z$ and $\xi\delta\eta/\delta z$ leads to a phase transition with an IC structure.

Recently McConnell and Heine[17] have developed a macroscopic approach for the description of IC transitions in insulators. The theory is based on the existence of a subsidiary mode which can only have an interaction with the main mode at nonzero wave vector. Among the examples where their theory applies, the authors of Ref. 17 consider $NaNO_2$. There the lattice shear is the subsidiary mode.[10]

In the present paper, the lattice dynamical model of Ehrhardt and Michel[13] is extended and applied in order to study the IC transition in $NaNO_2$ from a microscopic point of view. The microscopic theory allows us to specify the meaning of the parameters that are relevant for the occurrence of an IC transition. In particular one thereby obtains precise information on the wave vector—and temperature dependence of the static order-parameter susceptibility which diverges at the IC transition. This allows us to study the temperature—and wave-vector behavior of the intensity of diffuse x-ray scattering and to explain the corresponding experiments[2] in the paraelectric phase when the temperature is decreasing towards the IC transition. We establish the connection between microscopic and macroscopic approaches by calculating the nonequilibrium free energy on the basis of the microscopic model. The present paper is divided in several sections.

In Sec. II the translation-rotation coupling is studied at finite wave vector $\vec{q}$. There exists a nonzero coupling to acoustic displacements and at small wave vector this coupling vanishes as q^2 for $\vec{q} \rightarrow 0$. The acoustic displacements refer to center-of-mass displacements per unit cell. They involve both the displacements of the Na atoms and of the centers of masses of the NO_2 molecules.

The bilinear coupling produces an effective orientational interaction between reorienting molecules. This lattice-mediated interaction (Sec. III) has to be considered in addition to the direct electrostatic dipole interaction between NO_2 groups. The combined effect of both interactions leads to resonances at finite wave vector in the orientational static susceptibility at the IC phase transition.

Next (Sec. IV) the nonequilibrium free energy is calculated in the framework of molecular-field theory from the microscopic model. It is shown that an instantaneous configuration of molecular orientations with a given spatial modulation leads to a corresponding configuration of acoustic displacements with a same modulation. A detailed discussion of the possibility of an IC transition is then given in Sec. V. Comparison is made with x-ray diffuse scattering experiments.[2] In Sec. VI we investigate the possibility of a lattice instability and the occurrence of a corresponding anomaly in the phonon dispersion law.

II. TRANSLATION-ROTATION COUPLING

We start with investigating the coupling of the orientational order parameter to acoustic lattice displacements at finite wave vector $\vec{q}$. In Ref. 13, Eq. (3.3), the following interaction potential has been obtained:

$$V = V^R + V^{TR} \ . \tag{2.1}$$

Here V^R is a sum of single-particle potentials for each NO_2 molecule at site $\vec{n}$, it represents a crystal-field term:

$$V^R = \sum_{\vec{n}} c_2 \cos[2\phi(\vec{n})] \ . \tag{2.2}$$

In Eq. (2.2), $\phi(\vec{n})$ denotes the rotation angle of the NO_2 molecule for rotations about the $\vec{c}$ axis while the O—O line is parallel to $\vec{c}$. The value $\phi = 0$ corresponds to an alignment of the molecule in the $\vec{b}$ direction. The second term on the right-hand side (rhs) of Eq. (2.1) stands for the bilinear translation-rotation coupling. Its general form [Eq. (3.13) of Ref. 13] reads

$$V^{TR} = \sum_{\vec{n},\vec{n}'} \sum_{j=1}^{3} \sum_{\alpha=1}^{2} v_{j\alpha}(\vec{\tau})\, Y_\alpha(\vec{n}') \times [u_j(\vec{n}', \mathrm{Na}) - \vec{u}_j(\vec{n}, D)] \ . \tag{2.3}$$

Here $\vec{\tau} = \vec{n}' - \vec{n}$ is restricted to nearest neighbors for a NO_2 molecule at site $\vec{n}$ surrounded by six Na atoms at site $\vec{n}'$. The integers $\vec{n}$ and $\vec{n}'$ measure lengths in units half the lattice constants. The crystal fixed Cartesian-coordinate system (components $j = 1, 2, 3$) is taken such that the x, y, and z directions correspond with the crystallographic axes $\vec{b}$, $\vec{a}$, and $\vec{c}$, respectively. In Eq. (2.3), $u_j(\vec{n}', \mathrm{Na})$ and $u_j(\vec{n}, D)$ denote the translational displacements of the Na atom and the $NO_2 \equiv D$ molecule away from their equilibrium positions $\vec{X}(\vec{n}')$ and $\vec{X}(\vec{n})$, respectively. D stands for the center of rotation of the NO_2 molecule. The rotational coordinates are given by four symmetry-adapted functions $Y_\alpha \equiv (\cos\phi, \sin\phi, \cos2\phi, \sin2\phi)$ for the molecule at site $\vec{n}$. As has been shown in Ref. 13, $\cos\phi$ and $\sin\phi$ are the components of the orientational order parameter.

Since the crystal field in $NaNO_2$ is strong,[13] $\cos\phi$ takes essentially the two extreme values $+1$ and -1 which correspond to orientations of the NO_2 molecule in positive and negative $\vec{b}$ direction. Then $\sin\phi$ is negligible. Here we are only interested in the coupling of the translations to the orientational order parameter. Therefore we retain only $Y_1 \equiv \cos\phi$ in Eq. (2.3) and drop the index α in Eq. (2.3):

$$V^{TR} = \sum_{\vec{n},\vec{n}'} \sum_{j} v_j(\vec{\tau})\, Y(\vec{n}) [u_j(\vec{n}', \mathrm{Na}) - u_j(\vec{n}, D)] \ , \tag{2.4}$$

where $Y_1(\vec{n}) \equiv \cos\phi(\vec{n})$. The coupling matrix

$v_{j\alpha}(\vec{\tau})$ was given in Ref. 13. Here we retain only the first column ($\alpha=1$). Explicitly

$$\underline{v}(\pm1,0,0)=\begin{pmatrix}M\\0\\0\end{pmatrix};\quad \underline{v}(0,\nu,\lambda)=\begin{pmatrix}C\\0\\0\end{pmatrix}\ , \tag{2.5}$$

where M and C are constants that follow from the microscopic steric-hindrance potential. In Eq. (2.5), the argument $(\pm1,0,0)$ refers to the interaction of the NO_2 group with the two neighboring Na atoms on the $\vec{b}\equiv x$ axis, the argument $(0,\nu,\lambda)$ with $\nu=\pm1$, $\lambda=\pm1$ refers to the interaction of the NO_2 group with the four neighboring Na atoms in positions $(0,\pm a/2,\pm c/2)$. We note that $\underline{v}(\vec{\tau})$ is symmetric with respect to inversion of $\vec{\tau}$.

We introduce Fourier transforms for the Na and NO_2 displacements:

$$\vec{u}(\vec{n},\kappa)=\frac{1}{\sqrt{Nm_\kappa}}\sum_{\vec{q}}\vec{u}(\vec{q},\kappa)\exp[i\vec{q}\cdot\vec{X}(\vec{n})]\ . \tag{2.6a}$$

Here $\kappa=\mathrm{Na}$ or D and m_κ is the corresponding mass. The total number of $NaNO_2$ units is N. Making use of $\underline{v}(\vec{\tau})=+\underline{v}(-\vec{\tau})$, we rewrite Eq. (2.4) as

$$V^{TR}=\sum_{\vec{q},\vec{\tau}}v_j(\vec{\tau})Y^\dagger(\vec{q})\left[\cos(\vec{q}\cdot\vec{\tau})\frac{u_j(\vec{q},\mathrm{Na})}{\sqrt{m_{\mathrm{Na}}}}-\frac{u_j(\vec{q},D)}{\sqrt{m_D}}\right]\ , \tag{2.7}$$

with

$$Y^\dagger(\vec{q})=\frac{1}{\sqrt{N}}\sum_{\vec{n}}Y(\vec{n})\exp[i\vec{q}\cdot\vec{X}(\vec{n})]\ . \tag{2.6b}$$

In Eq. (2.7) we use the summation convention over repeated indices j.

As was shown previously,[13] in the limit $\vec{q}=0$, Eq. (2.7) provides a coupling of the order parameter to optical modes while there is no coupling to acoustical modes. We shall now investigate the coupling to acoustic modes for finite wave vector $\vec{q}$. We consider primitive lattice cells with one NO_2Na unit and total mass $m=m_{\mathrm{Na}}+m_D$. The corresponding center of mass displacements have Fourier components

$$\vec{s}(\vec{q})=\left(\frac{m_{\mathrm{Na}}}{m}\right)^{1/2}\vec{u}(\vec{q},\mathrm{Na})+\left(\frac{m_D}{m}\right)^{1/2}\vec{u}(\vec{q},D)\ . \tag{2.8}$$

The acoustical part of the bilinear interaction (2.7) is then given by

$$V^{TR}_{\mathrm{ac}}=\sum_{\vec{q}}\hat{v}_j(\vec{q})Y^\dagger(\vec{q})s_j(\vec{q})\ . \tag{2.9}$$

Here we have defined the center-of-mass transformed coupling

$$\underline{\hat{v}}(\vec{q})=\frac{1}{\sqrt{m}}[\underline{v}(\vec{q})-\underline{v}(\vec{q}=0)]\ , \tag{2.10a}$$

with

$$v_i(\vec{q})=\sum_{\vec{\tau}}v_i(\vec{\tau})\cos(\vec{q}\cdot\vec{\tau})\ . \tag{2.11}$$

(For details of this calculation, the reader should consult Appendix A.) We rewrite Eq. (2.10a) as

$$\underline{\hat{v}}(\vec{q})=-\frac{2}{\sqrt{m}}\sum_{\vec{\tau}}\underline{\hat{v}}(\vec{\tau})\sin^2\left(\frac{\vec{q}\cdot\vec{\tau}}{2}\right)\ . \tag{2.10b}$$

We carry out the sum over $\vec{\tau}$ and use explicitly Eqs. (2.5). Only the first element in the 3×1 row matrix $\underline{\hat{v}}$ is different from zero. The result reads

$$\hat{v}_1(\vec{q})=-\frac{4}{\sqrt{m}}\left\{M\sin^2\left(\frac{q_xb}{2}\right)+C\left[\sin^2\left(\frac{q_ya+q_zc}{4}\right)+\sin^2\left(\frac{q_ya-q_zc}{4}\right)\right]\right\}\ . \tag{2.10c}$$

Within our simplified model, rotations of the NO_2 molecule around the $\vec{c}$ axis couple essentially with acoustic displacements in $\vec{b}$ (i.e., $\vec{x}$) direction. For a given direction $\vec{q}$ this coupling leads to a propagating wave of orientations and displacements. The modulated incommensurate structure corresponds to a freezing-in of such a mixed orientation-displacement wave.

Obviously this coupling matrix vanishes only for $\vec{q}=0$. At finite q there is a coupling to acoustic modes. Note however that this coupling vanishes as q^2 for small q. It is therefore different from the case of KCN, where we have a bilinear coupling between the orientational order parameter and acoustic displacements which is linear in q for small wave vector.[18] This difference is due to a different symmetry of the CN and the NO_2 molecules. It is most instructive to formulate the coupling of the orientations with acoustic translations in terms of strains ϵ. In the case of small wave vector, $qs\sim\nabla s\sim\epsilon$ where ∇ is the spatial gradient operator. The bilinear coupling in KCN is then of the form $V^{TR}\sim AY\epsilon$, i.e., a coupling between lattice strains and orientational order parameter, where A is a constant. On the other hand, Eq. (2.9) leads for small wave vector to a coupling of the form $V^{TR}\sim C\nabla Y\epsilon$, i.e., a coupling of lattice strains with the gradient of the order parameter,[17] where C is a constant. The bilinear interaction between translations and rotations leads to a lattice-mediated interaction between orienting NO_2 molecules. This interaction will be investigated in the next section.

III. ORIENTATIONAL INTERACTIONS AND SUSCEPTIBILITIES

In order to study the lattice-mediated interaction, we reconsider the potential Eq. (2.1) with V^{TR} replaced by V_{ac}^{TR} and add to it an elastic part

$$V_{\text{ac}}^{TT}=\sum_{\vec{q}}\tfrac{1}{2}M_{ij}s_i^{\dagger}(\vec{q})s_j(\vec{q}) \ . \tag{3.1}$$

We then have to consider the potential

$$U=V_{\text{ac}}^{TT}+V_{\text{ac}}^{TR}+V^{R} \ . \tag{3.2}$$

In Eq. (3.1) $\tilde{M}$ denotes the dynamical matrix for acoustical phonons. The calculation of such a matrix in the presence of rotational degrees of freedom is in itself a lattice dynamical problem and it has recently been treated for the case of the alkali cyanides.[19] Here we assume that this problem has been solved. In fact for $NaNO_2$, M can be directly obtained from neutron scattering data.[4]

The bilinear interaction V_{ac}^{TR} leads to an adjustment of the lattice to the instantaneous configuration of molecular orientations. For a given configuration $\{Y_\alpha^e(\vec{q})\}$, we minimize the rhs of Eq. (3.2) with respect to the displacement $s_i(\vec{q})$, thereby obtaining

$$s_i^e(\vec{q})=-M_{ij}^{-1}(\vec{q})\hat{v}_j(\vec{q})Y^e(\vec{q}) \ , \tag{3.3}$$

for the resulting acoustic lattice displacements. Here the superscript e denotes an instantaneous expectation value. In particular, expression (3.3) demonstrates that a freezing-in of a given pattern of orientations entails a corresponding freezing-in of lattice displacements. Orientations and displacements are characterized by a same wave vector $\vec{q}$.

Introducing expression (3.3) into Eq. (3.2), we find for the minimum of the potential

$$U_{\text{min}}=-\frac{1}{2}\sum_{\vec{q}}\underline{C}(\vec{q})Y^{e*}(\vec{q})Y^e(\vec{q})+V_R \ . \tag{3.4}$$

Here $\underline{C}(\vec{q})$ is the effective interaction matrix between orientationally ordered molecules:

$$\underline{C}(\vec{q})=\underline{\hat{v}}^{\tau}(\vec{q})\tilde{M}^{-1}(\vec{q})\underline{\hat{v}}(\vec{q}) \ . \tag{3.5}$$

Due to the simple structure of $\underline{\hat{v}}$, the matrix $\underline{C}$ has only one single element: $C_{11}=\hat{v}_1(M^{-1})_{11}\hat{v}_1$. The magnitude and direction of this interaction depend on the wave vector $\vec{q}$. The dynamical matrix $\underline{M}$ or equivalently the corresponding elastic constants are a measure of the lattice stability with respect to quasistatic long-wavelength deformations. The smallness of the elastic constants c_{66} expresses the softness of the lattice with respect to xy shear deformations.[5] Consequently the elastic Green's function $[(M^{-1}(\vec{q})]_{11}$ in Eq. (3.5) is most efficient in providing an effective, lattice-mediated interaction between reorienting NO_2 molecules for a wave vector $\vec{q}$ is in y direction (i.e., direction of the $\vec{a}$ axis). For $\vec{q}=(0,k,0)$, the dynamical matrix of the orthorhombic lattice is diagonal: In the long-wavelength limit it reads

$$M(k)=k^2[c_{66}^0,c_{22}^0,c_{44}^0]/\rho \ . \tag{3.6}$$

Here we have only quoted the three nonzero diagonal elements within the square brackets on the rhs of Eq. (3.6); c_{66}^0, c_{22}^0, and c_{44}^0 are the bare elastic constants. The material density ρ is given by $2m/V_z$, $V_z=abc$ is the volume of the orthorhombic unit cell. For the same wave vector, Eq. (2.10c) reads

$$\hat{v}_1(k)=-\left[\frac{8}{\sqrt{m}}\right]C\sin^2\left[\frac{ka}{4}\right]\approx-\frac{Ca^2k^2}{2\sqrt{m}} \ , \tag{3.7a}$$

and consequently Eq. (3.3) becomes

$$s_x^e(k)=\frac{\sqrt{m}\,aC}{bcc_{66}^0}Y^e(k) \ . \tag{3.8}$$

In a similar way, the lattice-mediated interaction (3.5) becomes in the long-wavelength limit

$$C_{11}(k)=\frac{k^2C^2a^3}{2c_{66}^0bc} \ . \tag{3.7b}$$

Note that the wave-vector dependence of this interaction is different from the case of KCN where in the long-wavelength limit the microscopic interaction[18] takes the form of an elastic dipole interaction,[20] as was shown in Ref. 21.

In order to discuss the orientational phase transition, we have to consider in addition to the lattice-mediated interaction also the electrostatic dipole-dipole interaction. This interaction, formulated in terms of an Ising spin model, has so far been considered[2,22] as the dominant interaction in $NaNO_2$. The general form of the electric dipole interaction is given by

$$V_{dd}=\frac{1}{2}\sum_{\vec{n},\vec{l}}\left[\frac{\vec{\mu}(\vec{n})\cdot\vec{\mu}(\vec{l})}{R^3}-\frac{3[\vec{\mu}(\vec{n})\cdot\vec{R}][\vec{\mu}(\vec{l})\cdot\vec{R}]}{R^5}\right] . \tag{3.9a}$$

Here $\vec{n}$ and $\vec{l}$ run over the equilibrium sites D of the NO_2 lattice with $\vec{R}\equiv\vec{X}(\vec{n})-\vec{X}(\vec{l})$. The dipole moment at site $\vec{n}$ is denoted by $\mu(\vec{n})$. In the present model, we consider only rotations around the $\vec{c}$ axis and assume that the crystal field along the $\vec{b}$ axis is strong. Then $\vec{\mu}$ has only one nonzero component:

$$\mu_x(\vec{n})=\mu\cos\phi(\vec{n})\equiv\mu Y(\vec{n}) \ , \tag{3.10}$$

where μ is the value of the dipole moment. The dipolar interaction then becomes

$$V_{dd}=\frac{1}{2}\sum_{\vec{n},\vec{l}}J(\vec{n},\vec{l})Y(\vec{n})Y(\vec{l}) \ , \tag{3.9b}$$

with

$$J(\vec{n},\vec{l})=\frac{\mu^2}{R^3}\left(1-\frac{R_x^2}{R^2}\right) \ . \tag{3.11a}$$

In Fourier-transformed form the interaction reads

$$V_{dd}=\frac{1}{2}\sum_{\vec{q}} Y^{\dagger}(\vec{q})J(\vec{q})\,Y(\vec{q}) \tag{3.12}$$

and

$$J(\vec{q})=\sum_{\vec{R}} J(\vec{R})e^{i\vec{q}\cdot\vec{R}} \ . \tag{3.11b}$$

In order to discuss the possibility of a structural phase transition, we now take into account the terms $U_{\min}$ and V_{dd} which are given, respectively, by Eqs. (3.4) and (3.12). The total orientational potential reads for a given orientational configuration $\{Y^e(\vec{q})\}$:

$$U=U_{\min}+V_{dd} \ . \tag{3.13}$$

The main effect of the strong crystal field V^R is to restrict the values of $\cos\phi\equiv Y$ to values near +1 or −1. This means[13] that the single-particle expectation value $\langle\cos^2\phi\rangle$ is close to one. Using the potential (3.13), we calculate the collective orientational susceptibility within the framework of molecular-field theory. The result reads

$$\chi^{RR}(\vec{q})\equiv\langle Y^{e*}(\vec{q})\,Y^e(\vec{q})\rangle/T=[T-K(\vec{q})]^{-1} \ , \tag{3.14}$$

where T is the absolute temperature (units $k_B=1$) and where the total orientational interaction $K(\vec{q})$ is given by

$$K(\vec{q})=C_{11}(\vec{q})-C_0-J(\vec{q}) \ . \tag{3.15}$$

In Eq. (3.15), C_0 is the self-interaction which is due to the Onsager reaction field.[23] In the present case it reads

$$C_0=\frac{1}{N}\sum_{\vec{q}} C_{11}(\vec{q})\geq 0 \ . \tag{3.16}$$

At decreasing temperature in the paraelectric phase, a transition occurs at the largest value of T such that $T=K(\vec{q})$. One realizes that it is essential to study the dependence of the orientational interaction $K(\vec{q})$ on the wave vector. More quantitative details are presented in Sec. V where we shall discuss the incommensurate phase transition.

IV. FREE ENERGY

In order to establish more closely the connection of the present lattice dynamical model for $NaNO_2$ with the ideas which have been developed in the phenomenological theories[14–17] we calculate the instantaneous nonequilibrium free energy of the present model. Here we only present the results of this calculation. For details the reader is referred to a paper by Courtens and the present author.[24] Corresponding to instantaneous expectation values of the secular variables $s_i^e(\vec{q})$ and $Y^e(\vec{q})$, the free energy is a functional of the form

$$\mathfrak{F}=\mathfrak{F}[s_i^e,Y^e] \ . \tag{4.1}$$

Here the superscript denotes the instantaneous expectation values.

The potential includes the elastic interaction, the acoustic part of the translation-rotation coupling, the single-particle term, and the dipole-dipole interaction

$$W=V_{\mathrm{ac}}^{TT}+V_{\mathrm{ac}}^{TR}+V^R+V_{dd} \ . \tag{4.2}$$

Here the four terms of the rhs are given, respectively, by Eqs. (3.1), (2.9), (2.2), and (3.9a). Rewriting Eqs. (2.41), (2.40b), and (2.51) of Ref. 24 in terms of the present variables and coupling matrices, we obtain in molecular-field approximation for the nonequilibrium free energy

$$\mathfrak{F}=F_{\mathrm{ph}}^{e}+F_R^0+\mathcal{V} \ . \tag{4.3}$$

Here the first term on the rhs stands for the harmonic phonon free energy

$$F_{\mathrm{ph}}^{e}=-\sum_{\vec{q},\nu}\left[\frac{1}{2}\hbar\omega_\nu(\vec{q})+T\ln n_\nu(\vec{q})\right] \ . \tag{4.4}$$

The phonon frequencies $\omega_\nu(q)$ are the eigenvalues of the dynamical matrix (3.1), and $n_\nu(\vec{q})$ is the Bose-Einstein distribution for phonons of energy $\hbar\omega_\nu(\vec{q})$. The second term on the rhs denotes the free energy corresponding to the single-particle potential

$$F_R^0=-T\ln Sp\exp(-V^R/T) \ . \tag{4.5}$$

Here Sp stands for the trace over the orientational states of the NO_2 molecules. Finally the last term in Eq. (4.3) is given by

$$\begin{aligned}\mathcal{V}=\sum_{\vec{q}}\Big\{&\frac{1}{2}s_i^{e*}(\vec{q})M_{ij}(\vec{q})s_j^e(\vec{q})\\ &+\hat{v}_1(\vec{q})s_i^e(\vec{q})\,Y^{e*}(\vec{q})\\ &+\frac{1}{2}[T+C_0+J(\vec{q})]\,Y^{e*}(\vec{q})\,Y^e(\vec{q})\Big\} \ .\end{aligned} \tag{4.6}$$

Here we have taken into account the fact that $\langle\cos^2\phi\rangle=\langle YY\rangle_0=1$. Note that in Eqs. (2.46b)−(2.51) of Ref. 24 the sign of $J_{\mu\nu}$ is wrong and has to be changed. In writing down expression (4.3) for $\mathfrak{F}$, we did not retain contributions from the kinetic energy of translations and rotations because these are not relevant for our present purpose. However we have explicitly taken into account the Onsager reaction field.

In order to find the minimum of the free energy, we take advantage of the fact that in $NaNO_2$, c_{66} are the elastic constants with the lowest value.[5] We therefore consider a transverse-acoustic wave, polarized in x direction ($\vec b$ axis) and propagating in y direction ($\vec a$ axis). Taking $\vec q = (0,k,0)$ we transform Eq. (4.6) by using the change of variables

$$s_x^e(k) = -M_{11}^{-1}(k)\hat v_1(k)Y^e(k) \ . \tag{4.7}$$

The result reads

$$V = \sum_k \tfrac{1}{2}(\chi^{RR})^{-1}Y^{e*}(k)Y^e(k) \ , \tag{4.8}$$

with

$$\chi^{RR}(k) = [T - C_{11}(k) + C_0 + J(k)]^{-1} \ . \tag{4.9}$$

This expression represents the collective orientational susceptibility, Eq. (3.14), for a particular wave vector: $\vec q = (0,k,0)$. We recall by Eq. (3.5) that $C_{11}(k) = \hat v_1(k)M_{11}^{-1}(k)\hat v_1(k)$, since $\underline{M}$ is diagonal for this particular choice of wave vector.

The meaning of Eqs. (4.7) and (4.8) becomes transparent by the following considerations. For a given configuration of orientations $\{Y^e(k)\}$, we minimize the free energy $\mathcal{V}$, given by Eq. (4.6), with respect to the displacements

$$\left|\frac{\delta\mathcal{V}}{\delta s_x^e(k)}\right|_o = 0 \ . \tag{4.10}$$

Here the subscript o indicates that the orientational configuration is kept fixed. As a result of Eq. (4.10), we obtain Eq. (4.7) which is also equivalent to Eq. (3.3). Equation (4.8) represents the minimum of the free energy obtained after adjustment of the acoustical lattice displacements Eq. (4.7) to a given orientational configuration. The implications of the result [Eqs. (4.8) and (4.9)] will be discussed in the next section.

In order to establish more closely the connection with the macroscopic approaches, we relate the center-of-mass displacements to the strain field $\epsilon(\vec q)$ by writing

$$\epsilon_{ij}(\vec q) = iq_i s_j(\vec q)/\sqrt{m} \ . \tag{4.11}$$

(Here and in the following we drop the superscript e.) Then Eq. (4.7) reads in the long-wavelength limit

$$\epsilon_{yx}(k) = \frac{aC}{bcc_{66}^0} ikY(k) \ . \tag{4.12}$$

Consequently the strain field is proportional to the gradient of the orientational order parameter. The bilinear coupling term in Eq. (4.6) now reads in the long-wavelength limit

$$\sum_k \hat v_1(k)s_x(k)Y^*(k)$$

$$= -\frac{Ca^2}{4}\sum_k [\epsilon_{yx}(ikY)^* + ikY\epsilon_{yx}^*] \ , \tag{4.13}$$

where ϵ_{yx} and Y depend on k. Expression (4.13) has the same form as the gradient terms which are introduced in the phenomenological theories.[14,17] In particular, in Ref. 17 a coupling between the primary order parameter and a subsidiary shear mode in $NaNO_2$ was inferred from experiment.[10]

V. INCOMMENSURATE TRANSITION

In order to discuss the possibility of an IC phase transition, one has to investigate the minimum of the free energy.[15] In the present problem, the free energy (4.8) is a bilinear form, the coefficients χ^{RR} of which depend on the wave vector and temperature. Expression (4.9) shows that for sufficiently high temperature, $\chi^{RR}(k,T)$ is positive for any value of k. The disordered phase where $Y^e(k) = 0$ for any k is then the one with the lowest free energy. The static susceptibility $\chi^{RR}(K,T)$ is a measure of order-parameter fluctuations.

For a more quantitative study, we specify the coefficients which enter Eq. (4.9) in the long-wavelength case. Keeping in mind Eq. (3.6), we write

$$M_{11}(k) = \alpha' k^2 \ , \tag{5.1}$$

where $\alpha' \equiv c_{66}^0\rho^{-1}$. Obviously $\alpha' > 0$. We also write

$$\hat v_1(k) \equiv 2\sigma k^2 \ , \tag{5.2}$$

where $\sigma = -Ca^2/4\sqrt{m}$ follows from Eq. (3.7a). For the dipolar interaction $J(k)$, we use an expansion of the form

$$J(k) = -d + \sigma k^2 + \gamma k^4 \ . \tag{5.3}$$

where $d > 0$, $\gamma > 0$, $\delta \leqslant 0$. This choice of coefficients follow from the numerical calculations of Yamada and Yamada[2] which have been confirmed independently by Grimm.[25] Making use of Eq. (4.9), we then write

$$(\chi^{RR})^{-1} \equiv y(k,T) = uk^4 + vk^2 + w \ , \tag{5.4}$$

where

$$u = \gamma, \quad v = \delta - 4\sigma^2/\alpha' \ , \tag{5.5a}$$

$$w = T + C_0 - d \ . \tag{5.5b}$$

At sufficiently high temperatures such that

$$v^2 - 4uw < 0 \ , \tag{5.6}$$

the secular equation

$$y(k,T) = 0 \tag{5.7}$$

has no solution. Then, since $u > 0$, the function $y(k,T)$ is always positive. This situation corresponds to the disordered phase: $Y^e(k) = 0$ for any value of k. In the disordered phase, for a given temperature

T, the susceptibility $\chi^{RR}(k)$ has a maximum at

$$k_m = \pm \left(\frac{-v}{2u} \right)^{1/2} = \pm \left(\frac{4\sigma^2 - \delta\alpha'}{2\alpha'\gamma} \right)^{1/2} . \tag{5.8a}$$

This requires $-v > 0$ or equivalently

$$4\sigma^2 - \alpha'\delta > 0 . \tag{5.8b}$$

With decreasing temperature, $\chi^{RR}(k)$ increases and becomes infinite at a temperature T_0 obtained from the solution of

$$v^2 - 4uw = 0 , \tag{5.9a}$$

i.e.,

$$T_0 = d - C_0 + \frac{(4\sigma^2/\alpha' - \delta)^2}{4\gamma} . \tag{5.9b}$$

The corresponding value of k is given by

$$k_0 = k_m , \tag{5.10}$$

where k_m is defined by Eq. (5.8a) with condition (5.8b). An equation of type (5.7) has been also discussed in the phenomenological theories[14,17] where one starts from an appropriate ansatz for the free energy. The present microscopic theory demonstrates that $NaNO_2$ fits into the general scheme which is assumed by the phenomenological theories. In addition it clarifies the physical meaning of the parameters which enter these theories. We remark that condition (5.8b) is less restrictive than the condition $\delta < 0$ which is required in Ref. 2. The presence of the bilinear coupling between rotations and translations makes the existence of a minimum in the dipolar interaction $J(k)$ for $k \neq 0$ [see Eq. (5.3)] no longer a necessary condition for the existence of an IC transition. Although the numerical calculations of the dipolar interaction[2] indicate that there is a minimum in $J(k)$, we remark that this minimum is extremely shallow. The numerical calculations have been performed for dipoles on a rigid lattice. We expect that the presence of thermal fluctuations in the lattice parameters destroys the stabilizing effect of such a shallow minimum.

It is straightforward to show that Eq. (5.8a) results from the condition

$$\frac{\delta K(k)}{\delta k} = 0 , \tag{5.11}$$

where K is the total orientational interaction defined by Eq. (3.15). Consequently k_m is independent of temperature if the microscopic parameters γ, α', δ, σ entering K are independent of temperature. Experiment shows however that the position of the maximum of χ^{RR} in the paraelectric phases shifts to lower values k_m with decreasing temperature.[2] Since $\alpha' \equiv c_{66}^0 \rho^{-1}$, an increase of c_{66}^0 with decreasing temperature leads to a decrease of k_m. However the variation of c_{66}^0 with temperature[5] is too small to account for the observed change in k_m. We also do not expect that the long-range dipolar forces are changing sufficiently fast with temperature, although in principle the dipolar forces are influenced by the fluctuations of the lattice.

In our opinion the temperature dependent of k_m arises from a temperature dependence of the bilinear coupling $\sigma \propto C$. The coupling parameter C has been derived from the repulsive interaction of the NO_2 molecule with the four surrounding Na atoms in the $(\vec{c}, \vec{a})$ plane.[13] Returning to Eq. (2.5), we consider the matrix element $v_{11}(0, \nu, \lambda) = C$, or equivalently

$$v_{11}(\vec{\tau}) = v_{11}(\vec{X}(\vec{n}', \mathrm{Na}) - \vec{X}(\vec{n}, D)) . \tag{5.12}$$

For each of the four vectors $\vec{\tau}$ with components $\pm(0, a/2, c/2)$, $\pm(0, a/2, -c/2)$, the element v_{11} has the same value C. There are two possible reasons for a variation of C with temperature.

Firstly, a change of lattice parameters due to thermal expansion leads to a change of the value of v_{11}. Taking the numerical values given by Kucharczyk in Ref. 26, for a and c, we have calculated the distance $|\vec{\tau}|$ for different temperatures. We find $|\vec{\tau}| = 3.247$ and 3.249 Å at $T = 164$ and 200 °C, respectively. Since the absolute value of C increases with decreasing $|\vec{\tau}|$, this variation of the lattice parameters leads to a slight increase in C and correspondingly also in k_m when T decreases from 200 to 164 °C. Consequently we conclude that the slight temperature variation of the lattice parameters does not account for the substantial decrease of k_m with decreasing temperature.

Secondly we investigate the influence of thermal fluctuations which lead to an effective smearing out of the lattice parameters about their equilibrium values. Neutron[4] and x-ray studies[11,27] reveal the importance of thermal fluctuations in $NaNO_2$. The root-mean-square amplitudes of vibrations of all particles in $NaNO_2$ are large (10% of $|\vec{\tau}|$) in the disordered phase. Their value increases with increasing temperature. These fluctuations correspond to instantaneous changes of $|\vec{\tau}|$ and therefore of the coupling parameter $v_{11} \equiv C$. In order to take this effect into account, we follow the established theory of strongly anharmonic crystals (for a review, see, e.g., Ref. 28). We are then led to replacing v_{11} at fixed values of the lattice parameters by the thermal average

$$\langle v_{11}(\vec{\tau}) \rangle = \int d\vec{r}\, v_{11}(\vec{\tau} - \vec{r}) g(\vec{r}) . \tag{5.13a}$$

Here $g(\vec{r})$ is the pair-correlation function which has to be calculated in the framework of the renormalized harmonic approximation:

$$g(\vec{r}) = \langle \delta(\vec{r} - \vec{u}(\vec{n}', \mathrm{Na}) + \vec{u}(\vec{n}, D)) \rangle . \tag{5.13b}$$

The temperature dependence of the fluctuations is now reflected in the temperature dependence of the coupling parameter $\langle v_{11} \rangle \equiv C(T)$. The qualitative argument is as follows. A fluctuation of a given amplitude which simultaneously decreases $|\vec{\tau}|$, increases simultaneously the absolute value of C. Due to the shape of the repulsive overlap potential, we easily see that this increase of C is larger in absolute value than the decrease of C which results from a simultaneous increase of $|\vec{\tau}|$ with a same amplitude. Therefore the coupling $C(T)$ should increase with increasing temperature. Since $C \propto \sigma$, it follows from Eq. (5.8a) that k_m decreases with decreasing temperature until it reaches the value k_0 at $T = T_0$. The decrease of the incommensurate wave vector k_0 with decreasing temperature which is observed by experiments[9,11,29] should also result from a decrease of the amplitude of fluctuations with decreasing temperature. Since we expect that the decrease of the amplitude of fluctuations has a different slope in the disordered and in the IC phase, we expect a different slope in the temperature variation of $k_m(T)$ and $k_0(T)$. A detailed analytical and numerical study of the influence on fluctuations on the IC transition will be published separately.

The existence of short-range interaction between neighboring NO_2 molecules has been previously proposed by Yamada and Yamada.[2] It was also suggested that thermal expansion would lead to a change of this short-range interactions and consequently to a variation of k_m (q_s in the notation of Ref. 2) with temperature. Our description is based on the short-range interaction which expresses the direct contact of the NO_2 group with the surrounding Na ions. The temperature variation of this interaction is mainly the consequence of thermal fluctuations rather than of the thermal expansion.

VI. LATTICE INSTABILITY

The coupling of acoustic displacements to the order parameter is essential for the occurrence of the incommensurate transition. Therefore we expect that this coupling will also manifest itself in the static displacement-displacement correlation function at the IC transition.

We examine again the free energy, Eq. (4.6). Now we consider the acoustic displacements as primary variables. For a given configuration of displacements $\{s_x^e(k)\}$, we minimize the free energy with respect to the orientations:

$$\left.\frac{\delta \mathcal{V}}{\delta Y^e(k)}\right|_o = 0 \ , \tag{6.1}$$

and obtain

$$Y^e(k) = -[T + C_0 + J(k)]^{-1} \hat{v}_1(k) s_x^e(k) \ . \tag{6.2}$$

Eliminating $Y^e(k)$, we find for the minimum of the free energy for the given configuration $\{s_x^e\}$:

$$V\Big|_o = \sum_k \tfrac{1}{2} D_{11}(k) s_x^e(k) s_x^e(k) \ , \tag{6.3}$$

where D_{11} is given by

$$D_{11}(k) = [1 + C_{11}(k)\chi^{RR}(k)]^{-1} M_{11}(k) \ . \tag{6.4}$$

Here $\chi^{RR}(k)$ is the collective orientational susceptibility which has been given in Eq. (4.9). The quantity $D_{11}(k)$ is the renormalized dynamical matrix. It can be directly related to the static displacement-displacement correlation function. From the free energy (6.3) we obtain the probability distribution function $\exp(-V/T)$. Using standard concepts of statistical physics,[30] we obtain immediately

$$\langle s^{e*}(k) s^e(k) \rangle = T / D_{11}(k) \ . \tag{6.5}$$

The left-hand side of this equation represents the static displacement-displacement correlation function in the presence of the coupling of acoustic displacements to molecular orientations. As a result of this coupling, the term $C_{11}\chi^{RR}$ appears in the denominator of $D_{11}(k)$, Eq. (6.4). Therefore a singularity of $\chi^R(k)$ at the incommensurate transition, $k = k_0$, $T = T_0$ leads to a vanishing of D_{11} or to a divergence in the static displacement-displacement correlation. This situation shows again that we have in $NaNO_2$ a phase transition of both order-disorder and displacive character.

In order to make the connection with the description of phonon anomalies related to IC transitions,[31] we use the fact that $D_{11}(k) \equiv \omega_{TA}^2(k)$, where ω_{TA} is the transverse-acoustic-phonon frequency in the presence of translation-rotation coupling. On the other hand, $M_{11}(k) \equiv \omega_0^2(k)$, where ω_0 is the bare TA-phonon frequency. In the present case where there exists a strong crystal field, the single-particle susceptibility is given by $\chi_0 = 1/T$. Using also Eq. (4.9), we then rewrite Eq. (6.4) as

$$\omega_{TA}^2(k) = \omega_0^2(k) \left[1 - \frac{\chi^0 C_{11}(k)}{1 + \chi^0 (J(k) + C_0)} \right] \ . \tag{6.6}$$

Consequently there should appear a dip in the dispersion law of the TA phonons at $T = T_0$ and $k = k_0$.

Phonon anomalies at incommensurate transitions have been known for several years, mainly in one-dimensional conductors such as KCP and tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).[31] There a phonon instability (giant Kohn anomaly)[32,33] is related to a simultaneous Peierls instability of the electrons near the Fermi surface.[34] One recognizes that the analytic structure of Eq. (6.6) is very similar to the corresponding expressions for the square of the phonon frequency in these electronic systems. In the translation-rotation coupled system, the modulation of the orientational order is the analog of the static periodic modulation of the conduction electron density (charge-density wave[35]) in one-dimensional solids.

Soft modes at IC transitions have been also discovered in insulators, in particular, in K_2SeO_4 (Ref. 36) and in thiourea.[37,38] However, in $NaNO_2$ the lattice instability described by Eq. (6.6) has not been found in the phonon dispersion law measured by neutron scattering.[4,29] We believe that this is due to the fact that neutron inelastic measurements at the IC wave vector correspond to regime of frequencies which are too high in comparison of the low frequency of the orientational relaxation mode in $NaNO_2$.[4,6] A detailed study of the dynamics of the present model is in preparation.

VII. CONCLUDING REMARKS

We have shown the lattice dynamical model of $NaNO_2$ which has been proposed by Ehrhardt and the present author[13] leads to a coupling of the orientational order parameter to acoustic lattice displacements at finite wave vector. The microscopic model describes the modulated structure in terms of positional rearrangements of both the Na and the NO_2 particles. In the paraelectric phase, an orientational density wave couples to a displacive density wave. The incommensurate phase transition is described as a freezing-in of such a mixed orientational order-displacive wave. We recall that the theory has been formulated (Sec. IV) in terms of nonequilibrium expectation values of orientational order and transverse-acoustic displacements. Both types of motion are modulated by a same IC wave vector.

By calculating the nonequilibrium free energy on the basis of the microscopic model, we have established the connection with macroscopic Landau-type theories.[14,17] The microscopic model confirms the basic assumptions of the phenomenological theory concerning the coupling of a primary order parameter to a subsidiary mode.[17] Since this coupling is the essential mechanism that derives the IC phase transition, the existence of a minimum in the Fourier-transformed dipole-dipole interaction[2] is no longer required.

The coupling is a function of lattice parameters. It is affected by thermal expansion and by thermal fluctuations which follow from lattice anharmonicities. We have concluded that thermal fluctuations lead to an increase of the effective orientational interaction with increasing temperature. This feature suggests an explanation of diffuse x-ray experiments by Yamada and Yamada.[2] The peaks in the diffuse x-ray intensities in the paraelectric phase shift to lower values of the wave vectcor k_m when the temperature is lowered towards the IC transition. It is likely that the temperature variation of the root-mean-square amplitudes of lattice displacements is also relevant for the understanding of the variation of the IC wave vector in IC phases in general.

Summarizing the present results, we have shown that the microscopic model describes the IC phase transition, that it confirms the basic assumptions of the phenomenological theories and that it allows a qualitative understanding of several experiments.

Among the problems we intend to treat in a future publication is a qualitative and quantitative description of the static and dynamic phenomena in the incommensurate phase.

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APPENDIX

We want to extract the coupling to acoustic displacements from the bilinear interaction between translations and rotations, Eq. (2.7). We introduce the space of six-dimensional displacements

$$\{u_\rho(\vec{q})\} \equiv \{\vec{u}(\vec{q},\mathrm{Na}),\ \ \vec{u}(\vec{q},D)\}\ , \tag{A1}$$

where $\rho = 1,2,3$ labels the three components $j = 1,2,3$ of the displacements $u_j(\vec{q},\mathrm{Na})$ while $\rho = 4,5,6$ labels the three components of $u_j(\vec{q},D)$. We define the 6×1 interaction matrix

$$\{v_\rho(\vec{q})\} = \begin{pmatrix} v_j(\vec{q})/\sqrt{m_{\mathrm{Na}}} \\ -v_j(\vec{q})/\sqrt{m_D} \end{pmatrix}\ , \tag{A2}$$

where $j = 1,2,3$ and where $v_j(\vec{q})$ is defined by Eq. (2.10). The interaction (2.7) is now rewritten as

$$V^{\mathrm{TR}} = \sum_{\vec{q}} v_\rho(\vec{q})\, Y^\dagger(\vec{q})\, u_\rho(\vec{q})\ , \tag{A3}$$

where summation is understood over repeated indices ρ, α. We introduce three six-dimensional basis vectors in the space of acoustic displacements

$$\vec{e}^{\,i} = \left[\delta_{ij}\left(\frac{m_{\mathrm{Na}}}{m}\right)^{1/2},\ \ \delta_{ij}\left(\frac{m_D}{m}\right)^{1/2}\right]\ , \tag{A4}$$

explicitly,

$$\vec{e}^{\,1} = \left[\left(\frac{m_{\mathrm{Na}}}{m}\right)^{1/2},0,0,\left(\frac{m_D}{m}\right)^{1/2},0,0\right]\ , \tag{A5}$$

etc. Then the Cartesian components of the acoustic displacements vector (2.8) are given by

$$s_i(\vec{q}) = \sum_p e_p^i u_p(\vec{q}) \quad (i=1,2,3) \ . \tag{A6}$$

Similarly we define the acoustic coupling matrix

$$\hat{v}_i(\vec{q}) = \sum_p e_p^i v_p(\vec{q}) \ , \tag{A7}$$

and obtain by using Eqs. (A2) and (A4)

$$\hat{v}_i(\vec{q}) = \frac{1}{\sqrt{m}}[v_i(\vec{q}) - v_i(\vec{q}=0)] \ , \tag{A8}$$

which is equivalent to the matrix equation (2.10a). The interaction potential of the orientational order parameter with acoustic displacements is now given by Eq. (2.9).

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