Domain-wall pinning in the incommensurate phase of sodium nitrite

M. Y. Choi
Department of Physics, Seoul National University, Seoul 151, Korea
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We study the successive phase transitions and the domain-wall pinning in a model for sodium nitrite crystals. We use the Hubbard-Stratanovich transform to derive the Landau-Ginsburg free-energy functional from a microscopic model. The obtained free energy has a quadratic gradient term, and displays behavior consistent with experiments. In particular there exists a free-energy barrier to the domain-wall motion, leading to the possibility of the pinning of domain walls. This intrinsic pinning is interpreted as the origin of the specific-heat anomaly and the hysteresis observed in recent experiments.

There exist a number of materials which exhibit successive transitions from a prototype to an incommensurate phase and then to a commensurate phase. A typical example in the field of ferroelectricity is sodium nitrite ($NaNO_2$), which is known to have an incommensurate antiferroelectric phase at temperatures between T_c ($\approx 163°C$) and T_n ($\approx 164.5°C$).[1] This antiferroelectric phase is characterized by an incommensurate modulation of the magnitude of the dipole moments. As the temperature is lowered from T_n, the period of this incommensurate modulation along the a axis increases until a commensurate ferroelectric phase appears via a first-order transition at T_c.[2]

Phenomenological theories which reproduce these features have been developed by several authors.[3] While these theories are based on Landau-type-model free-energy densities, a microscopic lattice dynamical model containing the translation-rotation coupling has also been proposed.[4] Since the crystal field in $NaNO_2$ is strong, this model essentially reduces to the Ising-spin description.[5,6]

In recent specific-heat measurements on $NaNO_2$ crystals, a small specific-heat anomaly with a marked hysteresis was observed at temperature T_i slightly above T_c.[7] The origin of this anomaly, as well as of the thermal hysteresis, was then attributed to the pinning of domain walls, possibly due to defects in the sample. Indeed it seems that the anomaly was more evident in γ-ray-irradiated samples which were expected to have many defects. It is, however, of interest to note that the anomaly was observed even in virgin crystals with presumably very few defects. This implies that the defect pinning solely cannot account for the anomaly, thus making it necessary to consider another mechanism for the domain-wall pinning.

The purpose of this paper is to investigate the domain-wall pinning in the incommensurate phase of $NaNO_2$ crystals and to provide a natural explanation for the specific-heat anomaly. We start with the Ising-spin description in which the microscopic parameters describing the effective short-range interactions can be determined by the experimental data. From this microscopic model, we derive the Landau-Ginzburg free-energy functional through the use of a Hubbard-Stratanovich transform.[8] It is shown that the obtained free energy has a term quadratic in the gradient of the order parameter. Such a class of free-energy functionals has been analyzed within the mean-field theory to reveal the possibility of successive phase transitions.[3,9] In particular the commensurate-incommensurate transition at T_c is of the first order, and due to the existence of a free-energy barrier the pinning of domain walls occurs slightly above T_c. This is in qualitative agreement with experiments if we associate the specific-heat anomaly with this intrinsic pinning of domain walls.

Consider the Ising-spin description of $NaNO_2$, where an Ising spin $s_i = \pm 1$ is assigned to the NO_2 dipole at site i according to its orientation along the $\pm b$ axis. The Hamiltonian is then given by

$$H = \frac{1}{2}\sum_{ij} J_{ij} S_i S_j, \tag{1}$$

with $J_{ij} = I_{ij} + D_{ij}$, where D_{ij} is the long-range dipole interaction, and I_{ij} is the effective short-range interaction including the translation-rotation coupling. The summation is over the sites of the body-centered orthorhombic lattice.

We now apply the Hubbard-Stratanovich transform to Eq. (1), and express the partition function in terms of continuous spin variables Φ ($K \equiv J/T$; Boltzmann constant $\equiv$ 1):

$$Z \equiv \mathrm{Tr}\, e^{-H/T} = \int D\Phi\, e^{-F(\Phi)}, \tag{2}$$

where

$$F(\Phi) = \frac{1}{2}\sum_{ij} \Phi_i (K^{-1})_{ij} \Phi_j - \sum_i \ln \cosh \Phi_i.$$

In the momentum space the free-energy functional $F(\Phi)$ takes the form

$$F(\Phi) = \frac{1}{2}\sum_q [K^{-1}(q) - 1]\Phi(q)\Phi(-q) + (1/12N) \sum_{qq'q''} \Phi(q)\Phi(q')\Phi(q'')\Phi(-q-q'-q'') + O(\Phi^6), \tag{3}$$

where N is the number of sites, and $K(q)$ and $\Phi(q)$ are the Fourier transforms of K_{ij} and Φ_i, respectively. Noting that the incommensurate modulation occurs in the direction of the a axis, we expand the interactions $I(q)$ and $D(q)$ near

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$q=0$ along the a axis:

$$I(q)=\alpha+\beta q^2+\gamma q^4,$$
$$D(q)=\delta+\epsilon q^2-\mu q^4, \tag{4}$$
$$J(q)=I(q)+D(q)\equiv a+bq^2-cq^4.$$

For the dipole interaction, our numerical calculations show that the coefficients δ, ϵ, and μ are all positive, in agreement with the data in Ref. 5. Equation (4) then leads to the continuum form of the free energy in the coordinate space, valid around the critical region ($T\approx a$):

$$F(\Phi)=\int dx\, f(\Phi)$$
$$f(\Phi)=[(T-a)/2a]\Phi^2+\tfrac{1}{12}\Phi^4 \tag{5}$$
$$-(b/2a)(d\Phi/dx)^2+(c/2a)(d^2\Phi/dx^2)^2,$$

where $\Phi(x)$ may be regarded as the order parameter, and the coordinate system has been chosen in such a way that the x axis coincides with the a axis of the crystal.

The free energy of the form (5) has been studied[9,10] to reveal interesting critical behavior including the Lifshitz point at $T-a=b=0$ ($c>0$).[11] In particular, when b is greater than zero, there exist three phases according to the temperature T. For $T>T_n=a+b^2/4c$, the null solution $\Phi=0$ minimizes the free energy [Eq. (5)], implying a disordered (paraelectric) phase. As the temperature is lowered, an incommensurate (antiferroelectric) phase appears via a second-order transition at T_n. The wave number q_c of the modulation in this incommensurate phase depends on the temperature, decreasing from $(b/2c)^{1/2}$ at T_n to $0.68(b/c)^{1/2}$ at $T_c=a-1.18b^2/c$. Below T_c the system is ferroelectric with the order parameter $\Phi=[3(1-T/a)]^{1/2}$. There exists discontinuity in the amplitude of the order parameter at T_c; the commensurate-incommensurate transition in this case is of the first order in agreement with experiments on $NaNO_2$ crystals.

With the measured values of (T_n, T_c, q_c) and with the numerical values of (α,β,γ), we can determine the parameters (a,b,c) describing the short-range interaction. If we further assume that the short-range interaction exists only between nearest neighbors and between next-nearest neighbors (i.e., neighbors along each axis), we get the relation

$$a=8I_0+2(I_a+I_b+I_c),$$
$$b=-(I_0+I_a), \tag{6}$$
$$c=(I_0+4I_a)/48,$$

where I_0 is the interaction strength between nearest neighbors, and I_a is that between neighbors along the a axis, etc.

An interesting feature in this case of the first-order commensurate-incommensurate transition is that near this transition there exists a local minimum of the free energy as a function of the domain-wall spacing. Thus there can exist a free-energy barrier to the motion of domain walls, leading to the possibility of the domain-wall pinning. This "intrinsic" domain-wall pinning, as first pointed out by Jacobs,[10] provides the natural source of the specific-heat anomaly as well as the thermal hysteresis observed in experiments. The temperature T_i below which the pinning occurs has been estimated:[10] $T_i=a-0.97b^2/c$. In the incommensurate phase the region over which the pinning occurs occupies the fractional temperature range

$$(T_i-T_c)/(T_n-T_c)\approx 0.15, \tag{7}$$

regardless of the values of interaction parameters. Although thermal fluctuations have been neglected in this simple mean-field analysis, Eq. (7) is quite consistent with experiments, which give values of the ratio in the range 0.09 (cooling)–0.23 (heating) due to the hysteresis.[7]

It should be noted that this intrinsic pinning is different in nature from the lattice pinning due to the discreteness effects.[12] In the latter case the lattice-pinning energy can be estimated by[13]

$$E_p\approx\int dx\cos(2\pi x)f(\Phi), \tag{8}$$

where the Poisson summation formula has been used. Substituting Eq. (5) with $\Phi(x)\approx\Phi_0\cos(q_c x)$ into Eq. (8) for the incommensurate phase, we obtain the result $E_p\approx 0$. Therefore discrete lattice effects are negligible in $NaNO_2$ crystals, and the lattice pinning is excluded.

Finally, as noted in Ref. 7, the decrease of the transition temperatures T_n, T_c, and T_i with the γ-ray dose can be explained by reduction of interactions due to the defects induced by irradiation. In particular, the prediction of this analysis in consistent with specific-heat measurements if, for example, we assume that the fractional changes of the short-range interaction parameters I_0, I_a, and I_b+I_c due to the γ-ray dose are comparable with each other.

In summary, we have used the Hubbard-Stratanovich transform to derive the Landau-Ginzburg free-energy functional for $NaNO_2$ crystals, thus establishing the connection between microscopic models and phenomenological approaches. The obtained free energy is characterized by the term quadratic in the gradient of the order parameter, and has a local minimum as a function of the domain-wall spacing. This leads to the intrinsic pinning of domain walls at the temperature slightly above the commensurate-incommensurate transition temperature, which provides a natural explanation of the specific-heat anomaly and the hysteresis observed in recent experiments. It has been also shown that the discrete lattice effects are negligible, and the lattice pinning does not occur.

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