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The theory of the multirelaxational response of incommensurable modulated phases in order–disorder systems

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Abstract. The response of incommensurable modulated phases is studied non-perturbatively in materials with the order–disorder type of phase transition. We introduce a mode-independent approximation for relaxation time and for interaction energy in the corresponding set of Bloch equations of excitation motion. Using a simplified envelope method enabled us to calculate the dynamic dielectric susceptibility of the incommensurate phase. Multirelaxational complex behaviour is found. The effective relaxation time behaviour qualitatively corresponds to that observed by Hatta in 1970 for NaNO_2 . It is a frequency-dependent quantity due to relaxation of dispersionless excitations. The static dielectric susceptibility critical index γ changes its value from unity above the transition from the paraphase to the incommensurate phase to one-half below this phase transition near to the lock-in transition. Low-frequency dynamic susceptibility behaviour shows enhanced losses.

1. Introduction

The dynamics of ferroelectrics and antiferroelectrics in which motion of some units is responsible for an order–disorder-type phase transition may be described by using pseudospin formalism [1]. The ferroelectric phase and the phase with a sinusoidal modulation in NaNO_2 were described by a simple Ising-like model in 1963; see [2]. As has been discussed, for example, in [3], the modulated sinusoidal structure may be stabilized below some critical temperature T_c if there exists a non-zero wave vector \mathbf{q}_0 maximizing the quantity $J_q = \sum_j J_{ij} \exp(i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j))$. Here the J_{ij} are the interaction energies between two units localized at lattice sites \mathbf{R}_i and \mathbf{R}_j . The dynamics of such a system is described in the simplest case by the Ising-like Hamiltonian. This Hamiltonian is related to those systems for which it was recently found that the response of the incommensurate phase may become very non-trivial at low frequencies [4], where, besides quasiparticle-like excitations, almost dispersionless bands of excitations are also predicted to exist. Within the framework of the Heisenberg model, the incommensurate phase is found to respond at very low frequencies $\omega \rightarrow 0$ in spite of the presence of a strong on-site magnetic anisotropy. The origin of such a response lies in the fragmentation of the excitation energy spectrum [4]. Such a picture was also found in several other model systems [4]. Corresponding properties in models based on the Ising-like Hamiltonians were not discussed until recently. As will also be shown in our paper this task is an interesting theoretical problem in itself. However the Ising-like model is appropriate for the description of a broad class of real ferroelectrics and antiferroelectrics of the order–disorder type [5]. It is therefore clear that a comparison of theoretical and experimental findings may be very useful.

The multirelaxation behaviour of the incommensurate phase within the Ising pseudospin model using the perturbation approach was studied recently [5]. Theoretical results and their qualitative comparison with experimental findings indicate the presence of non-trivial low-frequency behaviour in this type of system also. It was, however, concluded that a non-perturbative approach should be used to see whether dispersionless low-frequency excitations also change relaxation behaviour in this class of model. The present paper contains the results for such a non-perturbative approach. It represents a continuation of the recent work [6] where the model appropriate for the description of the Ising-like order–disorder phase transition, from a paraphase to an incommensurable modulated ordered phase, in NaNO_2 type materials was used to describe relaxational behaviour. Corresponding dynamic equations of the Bloch type were studied perturbatively. It was found that the complex dielectric susceptibility, as a function of frequency, displays multirelaxational behaviour due to the coupling of the homogeneous polar soft modes to higher-order modes. In the present paper we continue to study the model equations found in [6]. Due to their mathematically complex form (an infinite set of coupled second-order difference equations with non-constant coefficients), we introduce a mode-independent approximation. This enables us to find an approximate solution of the infinite number of coupled equations in the explicit form. On the basis of the closed formulae some physical properties may be studied more thoroughly within our simplified model. We discuss the low- and high-frequency properties of the dynamic susceptibility, critical behaviour of the static susceptibility and relaxation frequency behaviour in the incommensurate phase. A general form is found for the motion of the n th excitation mode in the modulated phase due to the external field. The dynamic dielectric susceptibility χ is then found from the equation for the homogeneous fluctuations and taking an appropriate limit to Q . In the zero-frequency limit the static susceptibility χ_0 is explicitly calculated. Decreasing temperature from high temperatures to the critical temperature T_c , the static susceptibility behaviour is of the known mean-field type:

$$\chi_0 \approx \frac{1}{T - T_0}.$$

However, decreasing the temperature further, far below T_c but still above T_0 , the critical behaviour of the static susceptibility changes to

$$\chi_0 \approx \frac{1}{\sqrt{T - T_0}}$$

within the modulated phase. The change of the critical index is due to change in the excitation spectrum of the incommensurable modulated phase with respect to the paraphase. The critical index γ changes its value from unity above to T_c to one-half. This is a new result, which should be tested experimentally. On the basis of the equations of motion, one can say that the response of the incommensurate structure consists of a sum of an infinite number of Debye-like relaxators with frequency distributions of their relaxation frequencies and Curie constants. New excitations—normal modes of the incommensurable modulated phase—are characterized by different relaxation times. These modes are contributing to the resulting susceptibility at the same frequency ω . We have found a continuum of states of excitation characterized by a continuously varying weighting, instead of the usual quasiparticle-like spectrum, characterized by a weight function consisting of a sum of singular delta terms characterizing the quasiparticle dispersions. We further show that lower and lower relaxation frequencies become active when the temperature decreases. The real

transition temperature from the incommensurate to the ferroelectric phase is slightly higher than the virtual para–ferrophase transition temperature T_0 . While zero-relaxation-frequency processes do not occur within our simplified model in the incommensurate phase, it follows from our calculations that the weight of low-frequency relaxation movements of pseudospins increases with decreasing temperature. Low- and high-frequency behaviour of both the real and imaginary parts of the dynamic susceptibility for $T > T_0$ was explicitly found. Both the imaginary and real parts of the susceptibility vanish in a power-like way when increasing frequency. Qualitatively such behaviour resembles the behaviour of a single Debye-like relaxator. In the last part of the paper we discuss the relation between our results and the results of experiments made by Hatta [16] for NaNO_2 . Below the transition to the incommensurate phase, a frequency dependence of the effective relaxation frequency is observed. Its behaviour as found in this paper corresponds qualitatively with that observed by Hatta: increasing frequency increases relaxation frequency. The temperature dependence also corresponds qualitatively to that observed.

2. The model

The description of the order–disorder type of phase transition is based on the pseudospin formalism. We will use a simple Ising model with competing interactions in one dimension. A discussion of the dynamic properties of the incommensurate phases described within this model has already been started in previous work [6]. In this section we would like to display the main model properties for reference purposes.

The model Hamiltonian H_T , which we will use, was described in [3] and is given by

$$H_T = -\frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z. \quad (1)$$

Here S_i^z are quantum operators describing pseudospin variables with eigenvalues $S_i^z = \pm \frac{1}{2}$ at lattice sites i , where $i = 1, \dots, N_{latt}$. For simplicity we study a s.c. lattice with N_{latt} sites in which each site represents a fluctuating unit (for example a hydrogen or deuterium bond). Classical order–disorder ferroelectrics and antiferroelectrics are described by our model assuming that the tunnelling energy [3] is neglected. Such a model is closely related to the ANNNI model [7]. Real materials of the KDP and NaNO_2 type are characterized by more complicated structures and are described by more complicated models [8, 9]. Study of our simplified model may give results which enable us to qualitatively demonstrate the properties of expected new effects in real materials.

A simplification introduced into our model is to assume that the modulation occurs in the $(1, 0, 0)$ direction only. The modulation wave vector amplitude $Q = Q \cdot \mathbf{a}$, where \mathbf{a} is the basic lattice vector in the $(1, 0, 0)$ direction, is determined by the free-energy minimization. The Fourier transform of the interaction energy $J(q)$ is assumed to have the form

$$J(\mathbf{q}) = 2J_1 \cos(\mathbf{q} \cdot \mathbf{a}) + 3J_2 \cos(2\mathbf{q} \cdot \mathbf{a}) + 2J_k (\cos(\mathbf{q} \cdot \mathbf{b}) + \cos(\mathbf{q} \cdot \mathbf{c})). \quad (2)$$

The interaction energy constants J_1 and J_2 describe interactions between the nearest and next-nearest neighbours, respectively, in the modulation direction \mathbf{a} , and J_k describes interactions between the nearest neighbours in the (\mathbf{b}, \mathbf{c}) plane perpendicular to the modulation direction.

Below some temperature given by

$$kT_c \equiv \frac{J(Q)}{4} \quad (3)$$

the single plane-wave-modulated state

$$\langle S_n^z \rangle = S \cos(Qn + \phi) \quad (4)$$

is realized. S is the amplitude of the single plane wave, and ϕ is an arbitrary phase constant. The amplitude Q of the modulation vector \mathbf{Q} , where $\mathbf{Q} \perp \mathbf{b}, \mathbf{c}$ and $\mathbf{Q} \parallel \mathbf{a}$, is found to be given by

$$\cos(Q) \equiv -\frac{J_1}{4J_2}. \quad (5)$$

The amplitude of the basic harmonics, S , depends on temperature in the mean-field style:

$$S^2 \equiv \frac{T^3}{T_c^3} \left(\frac{T_c}{T} - 1 \right). \quad (6)$$

Validity of (6) is restricted to temperatures which are not very low with respect to the transition temperature where the single plane wave dominates. In the vicinity of the critical temperature T_c the amplitude behaves in the known mean-field style:

$$S^2 \equiv \left(1 - \frac{T}{T_c} \right).$$

Here and in the following, we assumed for simplicity that the modulation wave vector amplitude Q leads to the incommensurate single-plane-wave-modulated phase. We will not discuss the effects of the lock-in energies.

Our aim is to study the response of the incommensurate modulated state, in the order-disorder system described above, to small external fields $E_i(t) = E_i \exp(i\omega t)$. The dynamics of the excitations will be studied using the Bloch equations of motion as described in [3] (see, e.g., equation (5.78) of [3]). Small fields generate small perturbations of the equilibrium state. The mean value of the pseudospin S_i^z at site i , $\langle S_i^z \rangle_t = \langle S_i^z \rangle + \delta \langle S_i^z \exp(i\omega t) \rangle$, is given by

$$i\omega \delta \langle S_i^z \rangle = -\frac{1}{T_1} \left(\delta \langle S_i^z \rangle - \frac{\beta}{4} (1 - 4 \langle S_i^z \rangle^2) \right) \sum_j J_{ij} \beta \langle S_j^z \rangle - \frac{\beta}{2} (1 - 4 \langle S_i^z \rangle^2) \mu E_i. \quad (7)$$

Here T_1 is the longitudinal single-site relaxation time. The usual linearization procedure is based on an approximation in which the quadratic $\langle S_i^z \rangle^2$ terms in (7) are neglected. This step is correct for ferroelectric and antiferroelectric systems not far below the critical temperature at which a non-zero amplitude S develops. For systems in a state modulated with a non-zero wave vector different from those at the Brillouin zone boundary, this approximation would be too crude a simplification. The presence of the quadratic terms leads to the coupling of different paraphase normal modes below the critical temperature. New normal modes of excitation in the ordered phase may have qualitatively different energy spectra. This is why we consider the equation of motion (7) beyond the linear approximation.

The Fourier transform of equation (7) gives, after some algebraic manipulations, an infinite set of equations if the wave vector Q is incommensurate with the underlying lattice. It is convenient to introduce notation which simplifies the form of this set to

$$a_n S_n + b_{n-1} S_{n-1} + b_{n+1} S_{n+1} = c e_n + g e_{n-1} + g e_{n+1} \quad (8)$$

where n is any integer, $\beta \equiv 1/k_B T$:

$$\begin{aligned} a_n &= \left(i\omega + \frac{1}{T_1} - \frac{\beta J(q + 2nQ)}{4T_1} (1 - 2S^2) \right) \\ b_n &= \frac{\beta S^2}{4T_1} J(q + 2nQ) \quad c = \frac{\beta \mu}{2T_1} (1 - 2S^2) \quad g = -\frac{\beta \mu}{2T_1} S^2 \\ E_n &= E_{q+2nQ} \equiv \frac{1}{N_{latt}} \sum_l \exp(i(q + 2nQ)l) E_l \\ e_n &= E_n \exp(-i2\phi n) \\ s_n &= S_n \exp(-i2\phi n) \equiv \delta \langle S_{q+2nQ}^z \rangle \exp(-i2\phi n). \end{aligned} \quad (9)$$

Note that the wave vector q has its magnitude limited to the region $-Q < q \leq Q$. The quadratic terms mentioned above give terms S_{n+1} and S_{n-1} coupled to the term S_n . In other words, the paraphase normal modes corresponding to $q + 2(n+1)Q$ and $q + 2(n-1)Q$ couple to the mode with $q + 2nQ$ due to incommensurate modulation of the equilibrium state.

From (9) we see that an infinite set of paraphase normal modes are coupled in the incommensurate state. A homogeneous field also couples to an infinite number of paraphase normal modes. The case of a commensurate phase would correspond to a periodicity in the n -variable and thus would lead to a finite number of quasiparticle bands. The incommensurate case fluctuation spectrum is much more complex in the exact mathematical sense, as will be discussed in the next section.

3. A simplified model: mode-independent approximation

Let us consider those systems in which the maximum magnitude of the interaction energy, $J(Q)$, driving the paraphase to the modulated phase, is slightly higher than the lowest interaction energy $J(0)$, which ‘prefers’ the ferroelectric phase. Thus we consider physical systems in which the paraphase–ferrophase phase transition splits into at least two transitions: paraphase–incommensurate phase and incommensurate phase–ferrophase, and for which the temperature region in which the incommensurate phase exists is small with respect to the temperature at which the virtual phase transition, paraphase–ferrophase, would occur. Then we may introduce several approximations within the previously defined model which enable us to study a system of an infinite number of coupled equations (9) in a mathematically closed form. The solution which we obtain is, however, physically non-trivial and displays new features concerning the multirelaxational response of incommensurate modulated phases. We expect that, at least qualitatively, these new features may be observed under appropriate conditions.

The Fourier-transformed interaction energy $J(q)$ in (2) is assumed to have its maximum value at $q = Q$ corresponding to some modulated state. Its minimum value is expected to be at $q = 0$, corresponding to the ferroelectric state. Such a situation occurs for example in NaNO_2 [10]. The relative value of the difference between the two energies is equal to the relative value of the difference between the transition temperature from the paraphase to the modulated phase, T_c , and the virtual transition temperature from the paraphase to the ferroelectric phase, T_0 :

$$\delta \equiv \frac{J(Q) - J(0)}{J(0)} = \frac{T_c - T_0}{T_0}. \quad (10)$$

Taking into account that T_0 may be experimentally determined [10] from the paraphase relaxation frequency temperature behaviour or from static dielectric temperature behaviour it is possible to estimate the quantity δ for NaNO_2 : it is approximately of the order of 0.005. Whenever the quantity calculated in (10) is as small, the interaction energy $J(q)$, for any value of the wave vector q except $q = Q$, may be approximated (in the zeroth order in $(T_c - T_0)/T_0$) by $J(0)$ in the dynamic equation (9):

$$J(q) = J(0) + (J(Q) - J(0))(\delta_{q,Q} + \delta_{q,-Q}).$$

Such a substitution still preserves the static modulated ground state with $q = Q$ but simplifies the dynamic equations. The Fourier transform into direct space, with N the number of crystal planes in the modulation direction, gives

$$J(r - m) = J(0) \delta_{r,m} + \frac{2(J(Q) - J(0))}{N} \cos(Q(r - m))$$

which corresponds to an infinite-range effective oscillatory pseudospin–pseudospin interaction.

The single plane wave $S_n^z = S \cos(Q(r - m))$ still remains in the ground state, as may be easily verified. Note, however, that now

$$J(2nQ) = J(0)$$

for all non-zero integers n if Q takes an incommensurate value. It is reasonable to assume that, for those values of the system parameters for which the quantity (10) is small, the incommensurate phase may be practically characterized by the single-plane-wave regime: thus we neglect quantities of the order of $(T_c - T_0)/T_0$ and higher orders while we still consider fluctuations S_n of the order of $S^{|2n|}$. It is clear that our approach is more appropriate for temperatures not very far from the paraphase-to-incommensurate phase transition temperature. The approximation concerning the interaction energies, which we will use, leads to the following simplifications: (1) a mode-independent relaxation time; (2) mode-independent interaction energy; and enables a clear approach to incommensurability to be made via a limiting process using a sequence of commensurate phases.

3.1. Independent-relaxation-time approximation

The dynamic equations (9) are characterized by a set of the relaxation frequencies

$$\frac{1}{T_1} - \frac{\beta J(q + 2nQ)}{4T_1} (1 - 2S^2)$$

which correspond to different modes of fluctuations characterized by q and n . Due to a lattice-site-dependent interaction energy J , each mode is characterized by a different relaxation frequency in the incommensurate phase. Introducing an effective interaction energy $J(0)$, as described in the preceding subsection, a set of the above mentioned relaxation frequencies will be substituted for with a single relaxation frequency:

$$\frac{1}{T_1} - \frac{\beta J(0)}{4T_1} (1 - 2S^2).$$

The coefficients a_n from (9) take the same form for each mode:

$$a_n = \left(i\omega + \frac{1}{T_1} - \frac{\beta J(0)}{4T_1} (1 - 2S^2) \right) \equiv (i\omega + a)$$

which is a mode- (index n -) independent form. The physical background for this substitution is straightforward: the original set of different relaxation times is represented by the largest one.

3.2. Independent-relaxation-energy approximation

The dynamic equations (9) are further characterized by a set of interaction constants

$$b_n = \frac{\beta S^2}{4T_1} J(q + 2nQ)$$

which again correspond to different modes of fluctuation. Due to the space-dependent interaction energy J each two 'neighbouring' modes interact with different interaction energies in the incommensurate phase. Let us now introduce an effective interaction energy $J(0)$ as discussed above. Then the set of the interaction constants will be substituted for with a single interaction constant b . The coefficients b_n from (9) take the identical explicit form

$$b_n = \frac{\beta S^2}{4T_1} J(0) \equiv b$$

which is a mode- (index n -) independent form.

3.3. An approximation for the dynamic equations

We apply to our simplified model system a general time- and site-dependent electric field $E_i(t)$. The Fourier transform of equation (7) gives an infinite set of equations, and on assuming the mode-independent approximation as described above to hold the equations (9) take the form

$$(i\omega + a)S_n^0 + bS_{n-1}^0 + bS_{n+1}^0 = ce_n + ge_{n-1} + ge_{n+1}. \quad (11)$$

Let us write $\delta a_n = a_n - a$, $\delta b_n = b_n - b$ and $\delta S_n = S_n - S_n^0$. Here S_n is assumed to satisfy (9). Then the equations (11) become equivalent to the original equation (9), if we simultaneously solve

$$a_n \delta S_n + b_{n-1} \delta S_{n-1} + b_{n+1} S_{n+1} = -\delta a_n S_n^0 - b_{n-1} S_{n-1}^0 - b_{n+1} S_{n+1}^0. \quad (12)$$

Thus, our approximation in which we reduce (9) to the set of equations (11) is equivalent to neglecting equation (12) with respect to (11). In this paper we discuss only (11).

3.4. A sequence of commensurate phases

The infinite set of equations (11) may be easily solved using a limiting procedure in which the incommensurate phase with the modulation wave vector Q is approached by a sequence of commensurate phases with the modulation wave vectors $Q(L, M)$

$$Q(L, M) \equiv \frac{2\pi M}{L}$$

where

$$\lim_{M, L \rightarrow \infty} Q(L, M) = Q.$$

Now a procedure which leads easily to the solution of (9) consists in solving (11) for finite appropriate integers L and M , and then taking the above limit.

3.5. The solution for a general mode

Let us thus firstly assume that Q is commensurate, and given by a corresponding M and L . The solution of the equations (11) for modes S_n is searched for in the form of a Fourier expansion:

$$S_n = \sum_{\kappa=-L/2+1}^{L/2} \exp\left(i\frac{2\pi}{L}\kappa n\right) S_\kappa$$

for any value of momentum q . It is clear that the periodicity condition holds $S_{n+L} = S_n$. Directly from (11) we obtain

$$S_\kappa = \frac{1}{L} \sum_n \frac{(c + g e_{n-1} + g e_{n+1}) \exp(-i(2\pi/L)\kappa n)}{i\omega + a + 2b \cos(2\pi\kappa/L)}.$$

For the inverse form and the homogeneous field we obtain

$$S_n = \frac{1}{L} E \sum_\kappa \frac{(c + 2g \cos(2\pi\kappa/L))}{i\omega + a + 2b \cos(2\pi\kappa/L)} \exp\left(i\frac{2\pi}{L}\kappa n\right) S_\kappa \quad (13)$$

which is a general form for the motion of the n th mode due to the external field.

4. Dynamic and static susceptibility

The dynamic dielectric susceptibility χ is found from equation (13) for the homogeneous fluctuations $n = 0$ and taking an appropriate limit for Q . Assuming that the electric field perturbing the equilibrium state is the homogeneous field $E_i = E$ and using the definition for the susceptibility $\chi = 2\mu S_0/E$, where the zeroth mode S_0 is calculated from (13), we find

$$\chi = \frac{\mu N_{latt}}{\pi} \int_{-\pi}^{+\pi} \frac{(c + 2g \cos(x))}{i\omega + a + 2b \cos(x)} dx. \quad (14)$$

The real part of the dynamic susceptibility is then found to have the following form:

$$\chi' = \frac{\mu N_{latt}}{\pi} \int_{-\pi}^{+\pi} \frac{(a + 2b \cos(x))(c + 2g \cos(x))}{\omega^2 + (a + 2b \cos(x))^2} dx. \quad (15)$$

The imaginary part of the dynamic susceptibility is found to have the following form:

$$\chi'' = -\frac{\omega \mu N_{latt}}{\pi} \int_{-\pi}^{+\pi} \frac{c + 2g \cos(x)}{\omega^2 + (a + 2b \cos(x))^2} dx. \quad (16)$$

In the zero-frequency limit of (14), the static susceptibility χ_0 may be explicitly calculated. We have found the following explicit form:

$$\chi_0 = \frac{\mu^2 N_l}{k_B T} \frac{1}{\sqrt{(T - T_0)/T} \sqrt{(T - T_0)/T + 4S^2 T_0/T}} \left[1 - 2S^2 - \frac{T}{T_0} \left(\sqrt{\frac{T - T_0}{T}} \sqrt{\frac{T - T_0}{T} + \frac{4S^2 T_0}{T}} \right) - \left(1 - \frac{T}{T_0} (1 - 2S^2) \right) \right] \quad (17)$$

On decreasing the temperature above T_c , the static susceptibility behaviour, predicted from (17), is of the known mean-field type:

$$\chi_0 \approx \frac{1}{T - T_0}.$$

The critical index associated with the divergence of the static susceptibility in this temperature region is unity. On further decreasing the temperature below T_c (but still keeping it above T_0) the critical behaviour of the static susceptibility changes to

$$\chi_0 \approx \frac{1}{\sqrt{T - T_0}}$$

as may be easily shown from (17).

The critical index γ has now changed in value from unity, which is its value above T_c , to one-half. It is clear that by using scaling relations between different static and dynamic critical indices one may derive their new values. Due to lack of space this point is not considered in the present paper. Thus, our model predicts substantially different critical behaviour for the static susceptibility in the modulated region. We have displayed the behaviour of the inverse static susceptibility (17) in figure 1.

There is a local minimum around T_c which is then changed to a local maximum followed by a steep decrease. There is uncertainty concerning the experimental behaviour of the dielectric static susceptibility [10]. The values of the critical index which are reported are 1.11–1.24. These values are obtained from fits within the paramagnetic phase, where the dielectric static susceptibility departs from the mean-field behaviour, which occurs above 500 K only. Do interacting fluctuations of the forming incommensurate phase renormalize paraphase behaviour in a way corresponding to experiments? It is found here that the well known mean-field-type behaviour changes to another type of behaviour even within the mean-field-like approach taken here. It may be expected that other static and dynamic properties may also be renormalized with respect to those described using classical mean-field theories (see, e.g. [10] and references therein).

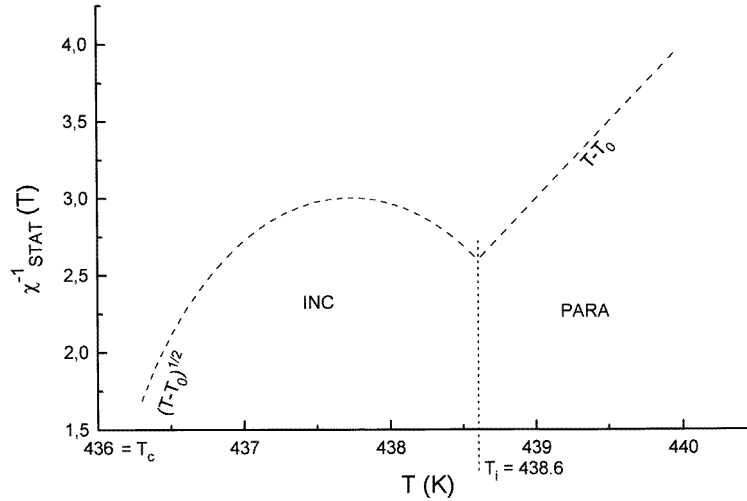


Figure 1. The behaviour of the inverse static susceptibility (17).

5. Dispersionless modes

On the basis of equation (14) one can say that the response of the incommensurate structure consists of a sum of an infinite number of relaxators with their relaxation frequencies:

$$\frac{1}{\tau_x} \equiv a + 2b \cos(x).$$

After substituting for constants a and b we obtain

$$\frac{1}{\tau_x} = \frac{T - T_0}{T_1 T} + \frac{T_0 S^2 \cos^2(x/2)}{T_1 T}.$$

Here the efficiency temperature T_0 is defined as $J(0)/(4k_B)$. The maximum value of the relaxation frequency is

$$\frac{T - (1 - S^2 T_0)}{T_1 T}.$$

The minimum value of this relaxation frequency is

$$\frac{T - T_0}{T_1 T}.$$

Both extremal values are the same when the temperature increases to the transition temperature T_c , where the amplitude S decreases to zero. Their difference reveals such behaviour explicitly:

$$\max \frac{1}{\tau_{eff}(x)} - \min \frac{1}{\tau_{eff}(x)} = \frac{S^2 T_0}{T_1 T}.$$

Thus the spread of relaxation frequencies which originates from interaction of modes increases on decreasing the temperature below the transition temperature.

The Curie constants take the form

$$\frac{\mu N_{\text{lat}}}{\pi} \frac{c + 2g \cos(x)}{a + 2b \cos(x)}.$$

Both of the resulting quantities (i.e. the relaxation frequency and the Curie constant) are now mode dependent—see their x -dependence.

The dynamic susceptibility may be written in the form

$$\chi = \chi_0 \int_{-\pi}^{+\pi} \frac{w(x)}{i\omega\tau_x + 1} dx \quad (18)$$

where χ_0 is the static susceptibility, and the weight of an x -relaxation mode contribution to the susceptibility is defined by

$$w(x) \equiv \frac{1}{2\pi\chi_0} \frac{1 + 2(q/c) \cos(x)}{1 + 2(b/a) \cos(x)}.$$

It is normalized to unity:

$$1 = \int_{-\pi}^{+\pi} w(x) dx.$$

The explicit form of the weight function is

$$w(x) \equiv \frac{1}{2\pi\chi_0} \frac{1 - [2S^2/(1 - 2S^2)] \cos(x)}{1 + [2S^2/(2S^2 - 1 + T/T_0)] \cos(x)}.$$

It is clear from this form that below the critical temperature and above the effective temperature T_0 there is no singular point in the weight function.

One may interpret the form (18) of the dynamic susceptibility as the sum of an infinite number of relaxation modes, each characterized by the label x , its density $w(x)$, and its relaxation frequency $1/\tau_x$. The independent-relaxation-time approximation as applied in section 3.1 approximates different relaxation times by the same time for the paraphase normal modes with the same wave vector \mathbf{q} and differing by the vector $2n\mathbf{Q}$. New excitations—normal modes of the incommensurable modulated phase—are characterized, as follows from (18), by different relaxation times. These modes are contributing to the resulting susceptibility at the same frequency ω . Note that we have found a continuum of states of excitations characterized by the continuously varying weighting $w(x)$ instead of a quasiparticle-like spectrum characterized by the weight function consisting of a sum of singular delta terms characterizing quasiparticle dispersions.

Such an interpretation of excitation spectra within our model is closely related to that for other similar systems made by Lovesey and co-workers [4, 11–13].

6. Square-root singularities

The imaginary part of the dynamic susceptibility may be easily transformed to the following form, which is more transparent:

$$\chi'' = -\frac{\chi_0\omega}{\pi} \int_{y_-}^{y_+} dy \frac{1}{\sqrt{(y_+ - y)(y - y_-)}} \frac{1 + 2g(2y - \delta_+)/\delta_-}{y^2 + \omega^2} \quad (19)$$

where

$$\chi_0 \equiv 2\mu N_{lat} \frac{c}{a} \quad \delta_{\pm} \equiv y_+ \pm y_-.$$

The form (19) was obtained from (14) by taking $y = a + 2b \cos(x)$.

The real part of the dynamic susceptibility may also be easily transformed to the more transparent form:

$$\chi' = \frac{\chi_0}{\pi} \int_{y_-}^{y_+} dy \frac{y}{\sqrt{(y_+ - y)(y - y_-)}} \frac{1 + 2g(2y - \delta_+)/\delta_-}{y^2 + \omega^2}. \quad (20)$$

From (19) and (20) we see that the weight $w(y)$ is proportional to the inverse square root:

$$w(y) \approx \frac{1}{\sqrt{(y_+ - y)(y - y_-)}}.$$

The first square-root singularity is localized at the point y_+ , which in its explicit form

$$y_+ = \frac{1}{T_1} \left(1 - \frac{\beta J(0)}{4k_B} (1 - 4S^2) \right)$$

does not depend on temperature, if we modify the mean-field form for the wave amplitude to

$$S^2 = \frac{1}{4} \left(1 - \frac{T}{T_c} \right)$$

instead of using the original form

$$S^2 = \left(1 - \frac{T}{T_c} \right).$$

Then y_+ takes the form

$$y_+ = \frac{1}{T_1} \left(1 - \frac{T_0}{T_c} \right).$$

The explicit form of the lower-root-singularity location obtained by steps similar to those followed in the case of the upper one is temperature dependent:

$$y_- = \frac{1}{T_1} \left(1 - \frac{T_0}{T} \right).$$

Note that both y_+ and y_- are positive for temperatures higher than T_0 . On decreasing the temperature towards T_0 the quantity y_- vanishes. Correspondingly, lower and lower relaxation frequencies become active when temperature decreases. The real transition temperature from the incommensurate to the ferroelectric phase is slightly higher than the virtual para-ferrophase transition temperature T_0 . This means that while zero-relaxation-frequency processes do not occur within our model in the incommensurate phase, it follows from our calculations that the weight of low-frequency relaxation movements of pseudospins increases with decreasing temperature.

7. Low-frequency behaviour, $T > T_0$

The low-frequency behaviour of both the real and imaginary parts of the dynamic susceptibility for $T > T_0$ may be easily found due to the fact that $y_- > 0$. The meaning of 'low frequency' is defined as referring to those frequencies for which the condition $\omega < y_-$ holds.

From (19) and (20) it follows that when the inequality above holds, both parts of the susceptibility may be expanded in powers of frequency:

$$\chi' \approx A - B\omega^2 + O(\omega^4) \quad \chi'' \approx C\omega - D\omega^3 + O(\omega^5).$$

We have found that constants A , B , C and D are given by

$$\begin{aligned} a &\equiv 1 - 2\frac{g}{c} \frac{y_+ + y_-}{y_+ - y_-} & b &\equiv 4\frac{g}{c} \frac{1}{y_+ - y_-} \\ A &\equiv I_2a + I_1b & B &\equiv I_4a + I_3b & C &\equiv I_1a + I_0b & D &\equiv I_3a + I_2b \\ I_0 &= 1 & I_1 &= \frac{1}{\sqrt{y_+ y_-}} & I_2 &= \frac{y_+ + y_-}{2(y_+ y_-)^{3/2}} \\ I_3 &= \frac{3(y_+ + y_-)^2 - 4y_+ y_-}{8(y_+ y_-)^{5/2}} & I_4 &= \frac{15(y_+ + y_-)^3 - 36y_+ y_- (y_+ + y_-)}{48(y_+ y_-)^{7/2}}. \end{aligned}$$

At a rough estimate, there are maximal losses at the frequency

$$\omega_e^2 \approx \frac{C}{3D}.$$

The halfwidth of the peak is

$$\text{HW} = \frac{2\omega_e}{\sqrt{3}}.$$

The effective relaxation frequency becomes frequency dependent:

$$\frac{1}{\tau_{eff}} \equiv \frac{\chi'\omega}{\chi''} \approx \frac{1}{\tau_{eff}}(0)(1 + \rho\omega^2)$$

where

$$\frac{1}{\tau_{eff}}(0) \equiv \frac{A}{C} \quad \rho \equiv \frac{B}{A} - \frac{D}{C}.$$

The effective relaxation frequency increases quadratically when frequency increases, at least at low frequencies and temperatures immediately below the transition temperature. We have estimated constants A , B , C and D from the explicit form of the corresponding integrals and found that

$$\frac{1}{\tau_{eff}} \approx \frac{1}{\tau_{eff}}(0) \left(1 + \alpha \left(\omega^2 \tau_{eff}^2(0) \right) \right) S^4. \quad (21)$$

The correction to the zero-frequency behaviour is of the order S^4 , in agreement with our previous perturbative calculations [5].

The zero-frequency effective relaxation frequency $(1/\tau_{eff})(0)$ is temperature dependent:

$$\frac{1}{\tau_{eff}}(0) = \frac{1 - T_1 \sqrt{\alpha^2 - 4b^2}}{\alpha/(\alpha^2 - 4b^2) - T_1}$$

where

$$\alpha \equiv \frac{1}{T_1} - \frac{\beta J(0)}{4T_1} (1 - 2S^2) \quad b \equiv \frac{\beta S^2}{4T_1} J(0).$$

The behaviour of the effective zero-frequency relaxation frequency below the transition temperature from the paraphase to the incommensurate phase is renormalized with respect to the paraphase behaviour given by

$$\frac{1}{T_1} - \frac{\beta J(0)}{4T_1}.$$

Note that around the transition point T_c we find

$$\frac{1}{\tau_{eff}}(0) \approx \alpha \approx (T - T_0)$$

and below this temperature point fluctuations above the ground state do not qualitatively change this temperature dependence, and

$$\frac{1}{\tau_{eff}}(0) \approx \alpha - 2b \approx (T - T_0).$$

A softening of the relaxation frequency below T_c continues from above this point; however, the proportionality coefficient is renormalized.

8. High-frequency behaviour, $T > T_0$

The high-frequency behaviour of both the real and the imaginary part of the dynamic susceptibility for $T > T_0$ may be easily found due to the fact that $y_+ > 0$ remains finite for the temperature region considered. ‘High frequency’ is defined as referring to those frequencies which satisfy the condition $\omega > y_+$.

From (19) and (20) we see that when the above inequality holds both parts of the susceptibility may be written in the form

$$\chi' \approx F \frac{1}{\omega^2} + O(\omega^{-4}) \quad \chi'' \approx G \frac{1}{\omega} + O(\omega^{-3}).$$

Here F and G are temperature-dependent constants. We see that both the imaginary and real parts of the susceptibility vanish in a power-like way with increasing frequency. Qualitatively such behaviour resembles the behaviour of a single Debye-like relaxator. The effective relaxation frequency becomes frequency independent now:

$$\frac{1}{\tau_{eff}} \equiv \frac{\chi' \omega}{\chi''} \approx \frac{F}{G}.$$

9. Discussion

Interactions of the homogeneous mode with higher-order modes due to an incommensurable modulated ground state change the usual single-mode-relaxation Debye-like behaviour of the paraphase to a more complicated behaviour. A multirelaxational character to the response is found. It should be present even in the single-plane-wave limit of the modulation; it is this single-plane-wave limit that is studied in this paper. One may argue in the same way as in [8] that results for the single-plane-wave limit also give a qualitatively correct picture for modulated states within which higher harmonics are present. Moreover the single-plane-wave limit leads to mathematical tractability. Note that in some materials—the compound NaNO_2 is a good example—there is no experimental evidence for the third and higher harmonics in the incommensurable modulation of the equilibrium state [10]. In the calculations above, an infinite number of modes coupled to the basic homogeneous one were considered. Their contributions to the dynamic susceptibility qualitatively change its behaviour. General forms of both the real and imaginary parts of the susceptibility were found in the closed form.

For a system of Ising spins close to its ordering temperature according to [10], it is generally expected that the order parameter dynamic susceptibility could be described in terms of a single Debye relaxation:

$$\chi(\mathbf{q}, \omega) = \frac{\chi(\mathbf{q}, 0)}{1 + i\omega\tau(\mathbf{q})}.$$

Suzuki and Kubo [14] have found that the relaxation time diverges at T_c for the critical wave vector of modulation. A monodispersive dielectric relaxation in the paraelectric phase in NaNO_2 was found in [15]. The Cole–Cole diagrams are characterized by the parameter $\beta = 0.94$ in the cited paper. The observed dispersion is seen to be close to the single-Debye-relaxation process. Below T_c one expects to observe two relaxation mechanisms with relaxation times corresponding to the amplitude and phase fluctuations [10]. Both relaxation times are expected to be frequency independent. Hatta [16] verified the validity of the single-Debye-relaxation model above T_c . He was able to fit his measurements to

$$\tau_{para} = 2.4 \times 10^{-8} (T - T_0)^{-1/3} \text{ s}.$$

The temperature T_0 is the same as the temperature found from the fit of the static susceptibility above T_c to the Curie–Weiss law. Below T_c an attempt to fit the relaxation time to a single effective relaxation time clearly indicates frequency dependence. While the temperature behaviour of the effective relaxation time resembles that of the phase relaxation [10], there is no reason for which the phase relaxation should dominate the dielectric response at $\mathbf{q} = \mathbf{0}$ of the modulated structure. The frequency dependence of the imaginary part of the complex dielectric constant in the temperature region of the modulated phase shows clearly (see [16], figure 1) that decreasing temperature shifts the weight of this part of the susceptibility to lower frequencies. Moreover, experiments carried out by Hatta in 1970 on NaNO_2 reveal immediately the frequency dependence of the effective relaxation frequency below the transition to the incommensurate phase. Its theoretical behaviour as found in our paper corresponds qualitatively with that observed by Hatta: increasing the frequency increases the effective relaxation frequency. Also the predicted temperature dependent qualitatively corresponds to that observed. However, the author failed to perform a more precise comparison of the theoretical predictions of this paper with the experimentally

observed dependences due to the absence of relevant measurements. It would be useful to produce a temperature–frequency diagram for the effective relaxation frequency and for the effective Curie constant, as an example. The value of the critical exponent γ would also be useful. Our theory predicts its change from the usual mean-field value to a new value of one-half. It would be interesting to perform the corresponding measurements on NaNO_2 as well as on other appropriate materials.

To summarize, we note that our model enables us to describe in a straightforward way the response of the incommensurate modulated phases in order–disorder systems. While a more detailed mathematical approach would predict the known Cantor-set type of the fragmented energy spectrum, it would be difficult to verify such a spectrum and its consequences in real materials. Our approach is based on Lovesey's idea of an envelope description of this energy spectrum and as such it certainly omits some features specific to Cantor sets. However, the independent-mode approximation used here is of predictive value: there are new predictions concerning the multirelaxational response of the incommensurate phase in materials with an order–disorder type of phase transition.

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