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Multirelaxation response of modulated phases in structural order–disorder systems

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Abstract. We study properties of multirelaxational phenomena originating due to interactions of modes in the incommensurate dielectrics of the order–disorder type described by the Ising-like model and the Bloch equations. Results found theoretically are discussed in relation to observed properties of some dielectric materials including NaNO_2 .

1. Introduction

In general one may expect that domain-like structures in incommensurate dielectrics, which are formed near the lock in transition to the lower ferroelectric phase, should be responsible, at least partially, for distribution of the relaxation times in the incommensurate structures. Regions of domain walls are non-uniform which, together with the motion of the domain walls themselves, is responsible for such an expectation: non-homogeneity leads to dynamically coupled normal modes. Non-homogeneity is also present in the single-plane-wave region. Thus one may there expect that the relaxations are also coupled. The domain wall region leads to more complicated equations for description of dynamics of modes, which however are similar to the single-plane-wave case. Thus one may expect that results of the single plane wave may be qualitatively extended to the domain wall regime. In this paper we consider the single-plane-wave regime only. What is the resulting picture of the response in the single-plane-wave region?

The response of the incommensurate phase may become very complex at low frequencies [1]: besides quasiparticle-like excitations dispersionless bands of excitations are expected to exist. The origin of such a response lies in the fragmentation of the excitation energy spectrum [1].

Dynamics of dielectrics in which motion of some units between a finite small number of states (typically two) is responsible for an order–disorder-type phase transition is usually described by using pseudospin formalism [2]. Indeed the phase transition between the ferroelectric phase and the phase with a sinusoidal modulation in NaNO_2 was described by an Ising-like model, see [3]. In general one can say [4] that the sinusoidal structure may be stabilized below some critical temperature T_c if there exists a non-zero wavevector q_0 maximizing the quantity $J_q = \sum_j J_{ij} \exp(iq \cdot (\mathbf{R}_i - \mathbf{R}_j))$. Here J_{ij} are 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 quantum Ising-like and Heisenberg-like Hamiltonians. Both models describe correctly also classical order–disorder structures at high temperatures. The excitation spectrum and response of the latter model was studied in [1] in the context

of magnetism. It was natural to extend the last-mentioned study to order-disorder-type materials described by the mentioned model Hamiltonians. Results of such an extension are described in [5].

The complex dynamical susceptibility was calculated using the Bloch equations. The perturbative and non-perturbative approaches enabled the authors to derive formulae for susceptibility which display multirelaxational behaviour due to the coupling of the homogeneous polar soft mode to higher-order modes. To increase the number of types of material in which the studied phenomena may be confronted with reality it is necessary to understand the qualitative and—if possible also—quantitative behaviour of these multirelaxational phenomena and compare the expected properties with those observed in related dielectrics. Results of some numerical studies of multirelaxation phenomena due to interaction of modes and their comparison with experimental behaviour in some dielectric materials are the main content of this paper. Results of the studies presented in [5] and in this paper may serve as a basis for at least qualitative discussion of observed multirelaxational phenomena in several dielectrics with incommensurate structures.

In the next section we display the main (mostly known) properties of the model which we study. In the third section some paraphase properties are described. They are useful for comparison with those of the incommensurate structure and serve for reference in the next sections of the paper. The last two sections are the main parts of this paper. The fourth section is devoted to the theoretical study of some properties of the incommensurate phase dynamics, namely the response of the structure as displayed by the complex susceptibility is described. In the last section we discuss results of the preceding sections in connection to some of the related dielectrics including NaNO_2 .

2. Model

The basic ingredients of the studied model Hamiltonian H_T were described in [4] and [5]. A similar model was used for the description of modulated structures in magnetism [6–12] and in dielectrics (NaNO_2 [13] and ANNNI model [14]). Let us recall the form of the model Hamiltonian which is given by

$$H_1 = -\frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z. \quad (1)$$

Here S_i^z are quantum operators describing pseudospin variables with eigenvalues $S_i^z = \pm \frac{1}{2}$ at lattice sites i , where $i = 1, \dots, N_{\text{latt}}$. We study a lattice with N_{latt} sites in which each site represents a fluctuating unit.

Real materials, for example of the KDP or NaNO_2 type, are characterized by more complicated structures and correspondingly are described by more complex models, [15] and [2]. We expect that our study of the simplified model may give results which will qualitatively demonstrate the expected effects in real materials.

For simplicity we shall assume that the modulation occurs in the single direction (1,0,0) only. The modulation wavevector amplitude $Q \equiv Q \cdot a$, where a is the basic lattice vector in the direction (1, 0, 0), is determined by the free energy minimization. The Fourier transform of the interaction energy $J(q)$ for q in the a direction is assumed to have the form:

$$J(q) = 2J_1 \cos(q \cdot a) + 2J_2 \cos(2q \cdot a) + 4J_{\text{perp}}.$$

The interaction energy constants J_1 and J_2 describe interaction between the nearest and next-nearest neighbours, respectively. The constant J_{perp} describes interactions in directions perpendicular to (1, 0, 0).

The random-phase-approximation-type analysis [4] of the basic part (1) of the Hamiltonian gives a description of the modulated state. The free energy is minimized at a given temperature T below some critical temperature T_c given by $kT_c = J(Q)/4$ for those mean values of the pseudospin operators which describe the single-plane-wave modulated state

$$\langle S_n^z \rangle = S \cos(Qn + \phi). \tag{2}$$

S is the small amplitude of the single plane wave, and ϕ is an arbitrary phase. The modulation vector Q is found to be

$$\cos(Q) = -\frac{J_1}{4J_2}. \tag{3}$$

The schematic phase diagram which shows regions of stability of the ferroelectric (F), antiferroelectric (A) and modulated phases (M) in the J_1, J_2 plane is given in figure 1.

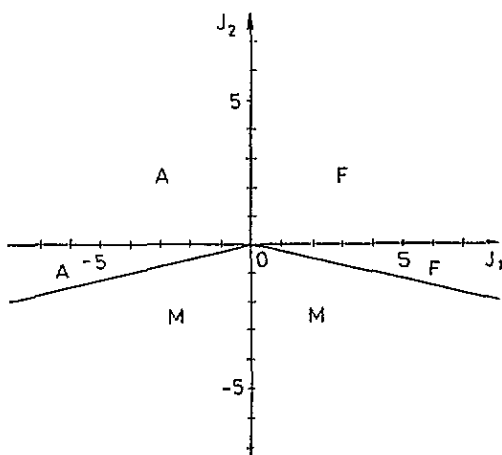


Figure 1. The schematic phase diagram in the J_1, J_2 plane: regions of stability of the ferroelectric (F), antiferroelectric (A) and modulated phases (M) are separated by the thick solid lines.

The wavevector Q is incommensurate in many dielectric materials, e.g. Rb_2ZnBr_4 may be characterized by $Q/2\pi \approx \frac{5}{17}$, see [16]. NaNO_2 may be characterized by $Q/2\pi \approx \frac{1}{8}$ immediately below T_c , see [17].

The dynamics of excitations was studied in [5] using Bloch equations for the motion of pseudospins. This method is thoroughly discussed in [4]. The explicit form of the equations of motion is

$$\begin{aligned} i\omega\delta\langle S_i^z \rangle = & -\frac{1}{T_1} \left[\delta\langle S_i^z \rangle - \frac{\beta}{4}(1 - 4\langle S_i^z \rangle^2) \right. \\ & \left. \times \sum_j J_{ij}\delta\langle S_j^z \rangle - \frac{\beta}{2}(1 - 4\langle S_i^z \rangle^2)\mu E_i \right] \end{aligned} \tag{4}$$

where $\delta\langle S_i^z \rangle$ are mean values of amplitudes of fluctuating pseudospin at site i given by $\langle S_i^z \rangle_t = \langle S_i^z \rangle + \delta\langle S_i^z \rangle \exp(i\omega t)$, see [4]. Furthermore, μ is the dipole moment of the elementary unit and T_1 is the longitudinal high-temperature relaxation time. The molecular field H_i at site i is given by

$$H_i = \left(0, 0, \sum_j J_{ij}\langle S_j^z \rangle \right) \equiv (0, 0, H_i). \tag{5}$$

A general time- and site-dependent electric field $E_i(t)$ is applied to our system at the equilibrium state (2). An infinite set of equations is found introducing the Fourier transform of (4)

$$a_n S_n + b_{n-1} S_{n-1} + b_{n+1} S_{n+1} = c e_n + g e_{n-1} + g e_{n+1} \quad (6)$$

where n is an integer, $\beta \equiv 1/k_B T$, and where

$$\begin{aligned} a_n &= \left(i\omega + \frac{1}{T_1} - \frac{\beta J(q + 2nQ)}{4T_1} (1 - 2S^2) \right) \\ b_n &= \frac{\beta S^2}{4T_1} J(q + 2nQ) \\ c &= \frac{\beta \mu}{2T_1} (1 - 2S^2) \\ g &= -\frac{\beta \mu}{2T_1} S^2 \\ E_n &= E_{q+2nQ} \\ e_n &= E_n \exp(-i2\phi n) \\ S_n &= \delta \langle S_{q+2nQ}^z \rangle \exp(-i2\phi n). \end{aligned} \quad (7)$$

From (7) we see that the uniform field is indirectly coupled to an infinite set of interacting normal modes in the incommensurate phase. The fluctuation spectrum in the incommensurate case, described by (7), is much more complex in the exact mathematical sense than in the commensurate case.

3. Paraphase

For reference purposes let us discuss the response of the paraphase. Above the critical temperature T_c , mean values of the pseudospins are zero. The dielectric susceptibility, which is in general defined here as

$$\chi = \left(2\mu \sum_i \delta \langle S_i^z \rangle \right) / N_{\text{latt}} E$$

for a homogeneous electric field with amplitude E , takes for the paraphase the well known form ($q = 0$):

$$\chi_{\text{para}} = \frac{(\mu^2 / T_1 k_B T)}{i\omega + (1/T_1)(1 - J(0)/4k_B T)}. \quad (8)$$

The usual Debye-relaxation-type behaviour is found.

Numerical values of the parameters used in our model calculations here are appropriate to model NaNO_2 , where the nearest-neighbour interactions in the modulation direction are ferroelectric, $J_1 \approx 81$ K, the next-nearest-neighbour ones are antiferroelectric, $J_2 = -26$ K, and the nearest-neighbour interactions in the directions perpendicular to the modulation direction are ferroelectric, $J_{\text{perp}} = 410$ K. To estimate these values of interaction constants we have used values [17] of the critical temperature $T_c = 438.69$ K, the Curie-Weiss temperature associated with the direct para-ferroelectric (virtual) transition is $T_0 = 437.41$ K and the high-temperature relaxation time constant is estimated to be $T_1 = 0.7922$ K $^{-1}$. The corresponding δ parameter takes the value $\frac{1}{8}$. Note that the transition temperature for the incommensurate to ferroelectric phase transition is 436.24 K. We use also the definition of the virtual transition temperature: $kT_0 = J(0)/4$. The last-mentioned temperature is identified

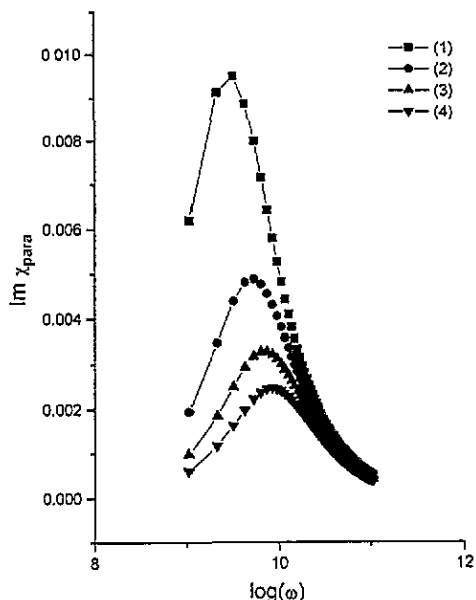


Figure 2. The frequency dependence of the imaginary part of the paraphase susceptibility for four temperatures: NaNO_2 with $\delta = \frac{1}{8}$ and temperature $T_c = 438.69$ K; $T_c + 50$ K (1), $T_c + 100$ K (2), $T_c + 150$ K (3), $T_c + 200$ K (4).

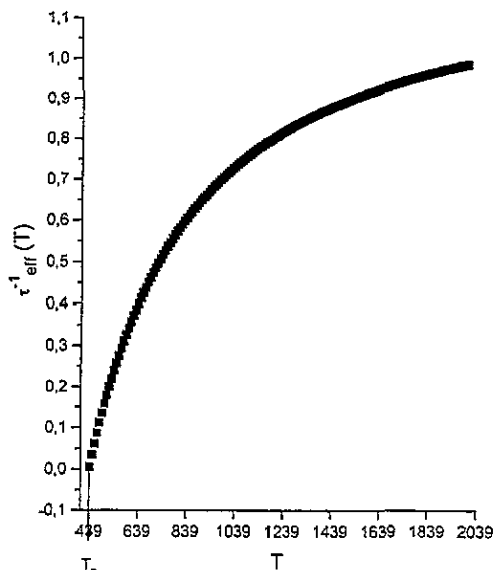


Figure 3. The temperature dependence of τ_{eff}^{-1} above the critical temperature T_c for NaNO_2 with $\delta = \frac{1}{8}$.

with the critical temperature observed in the static dielectric constant measurements and in the paraphase relaxation frequency behaviour. In figure 2 the frequency dependence of the imaginary part of the paraphase susceptibility for four temperatures in NaNO_2 with $Q/2\pi \equiv \delta = \frac{1}{8}$ and temperature $T_c = 438.69$ K is shown. With increasing temperature the corresponding curves at $T_c + 50$ K (1), $T_c + 100$ K (2), $T_c + 150$ K (3) and $T_c + 200$ K (4) change their shape. Note that the curves do not mutually intersect in the displayed frequency region. Note that the height of the peak increases with decreasing temperature. The peak frequency and the halfwidth of the peak slightly decrease with decreasing temperature: the two quantities are proportional to each other; the proportionality coefficient is $2\sqrt{3}$.

The paraphase relaxation time τ_{para} is given by

$$\frac{1}{\tau_{\text{para}}} = \frac{1}{T_1} \left(1 - \frac{J(0)}{4k_B T} \right).$$

At high temperatures this relaxation time is equal to the longitudinal relaxation time T_1 . The effective relaxation time τ_{eff} is equal to the inverse frequency at which $\text{Im } \chi$ has a peak when the dynamics is characterized by the single-relaxation-mode behaviour. Later we shall discuss how the effective relaxation frequency may be defined when the system is characterized by at least two relaxation modes.

In figure 3 we display the temperature dependence of τ_{eff}^{-1} above the critical temperature T_c . We see that there exists a decrease from its high-temperature value $1/T_1$ to the value $(1/T_1)(1 - T_0/T_c)$ at T_c . For NaNO_2 , in which $J(0) > 0$, this behaviour corresponds to that observed by Hatta [18, 19]. Note that in general interactions between pseudospins modify the paraphase relaxation time if $J(0) \neq 0$.

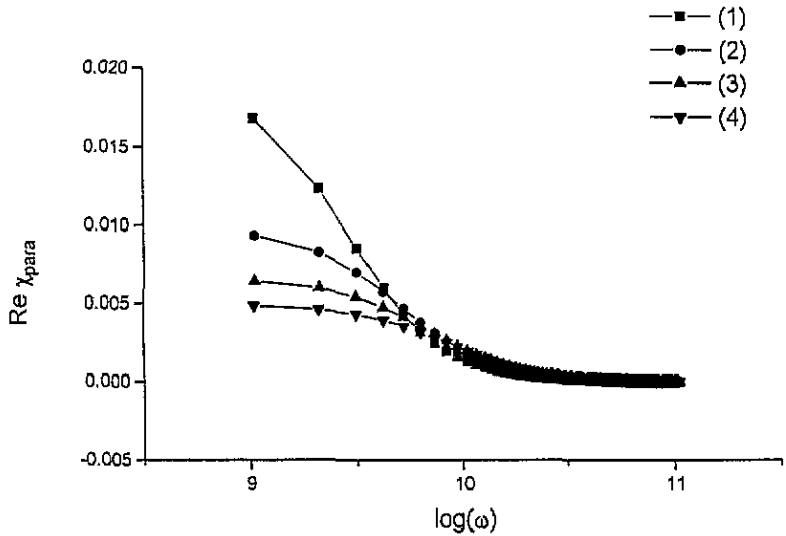


Figure 4. The frequency dependence of the real part of the paraphase susceptibility for four temperatures: NaNO_2 with $\delta = \frac{1}{8}$ and temperature $T_c = 438.69$ K; $T_c + 50$ K (1), $T_c + 100$ K (2), $T_c + 150$ K (3), $T_c + 200$ K (4).

The frequency dependence of the real part of the susceptibility is displayed in figure 4 for four temperatures in NaNO_2 with $\delta = \frac{1}{8}$ and temperature $T_c = 438.69$ K; $T_c + 50$ K (1), $T_c + 100$ K (2), $T_c + 150$ K (3), $T_c + 200$ K (4).

At frequencies higher than the peak frequency there exists almost no temperature change. At lower frequencies the real part of the susceptibility increases with decreasing temperature.

4. Incommensurate phase

Let us now discuss the behaviour of the complex susceptibility in the form appropriate for comparison with experiments. Below the critical temperature T_c , the dielectric susceptibility behaviour is modified due to the modified equilibrium state leading to modified excitations. Not very far from T_c the pseudospin amplitude mean value is small. In this temperature region it is convenient to use a perturbation analysis to describe influence of the modulated equilibrium state on the response of the system. We use the amplitude of the order parameter S as the perturbation parameter.

Let us first neglect coupling of the $q = 0$ mode to other modes in (7). This coupling would be absent in the uniform equilibrium state. The dielectric susceptibility behaviour is found to be

$$\chi_{\text{inc}} = \frac{\mu^2(1 - 2S^2)/T_1 k_B T}{i\omega + 1/T_1 - [\beta J(0)/4T_1](1 - 2S^2)}. \quad (9)$$

This equation describes a Debye-relaxation-type dispersion. The C constant in χ_{inc} (9) is modified with respect to its paraphase value by the factor $(1 - 2S^2)$ which decreases with decreasing temperature. We note that for the uniform phase (with $Q = 0$) two in this factor should be replaced by four.

If the value of the modulation wavevector Q is commensurate, the lock-in energy becomes essential and a finite number of modes $S_{0,\pm 1,\dots}$ would contribute to the susceptibility. If Q takes the incommensurate value then theoretically all higher-order terms

will contribute to the susceptibility. The dielectric susceptibility of the incommensurate phase up to the fourth order in S has the form [5]

$$\frac{\chi_4}{2\mu} = \frac{\chi_{\text{para}}}{2\mu} - S^2 \left(\frac{c_1}{\alpha_0} + \frac{c_0\beta_0}{\alpha_0^2} \right) + S^4 \left(\frac{c_0\beta_0^2}{\alpha_0^3} \right) - \frac{gb_1}{\alpha_0\alpha_1} - \frac{gb_{-1}}{\alpha_0\alpha_{-1}} + \frac{c_0b_0b_1}{\alpha_0^2\alpha_1} + \frac{c_0b_0b_{-1}}{\alpha_0^2\alpha_{-1}} + O(S^6) \tag{10}$$

where

$$\begin{aligned} \alpha_n &= \left(i\omega + \frac{1}{T_1} - \frac{\beta J(q + 2nQ)}{4T_1} \right) \\ \beta_n &= \frac{\beta J(q + 2nQ)}{2T_1} \\ a_n &= \alpha_n + S^2\beta_n \\ c_0 &= \frac{\beta\mu}{2T_1} \\ c_1 &= \frac{\beta\mu}{T_1} \\ c &= c_0 - c_1S^2. \end{aligned} \tag{11}$$

Let us note that the expansion in powers of S^2 is valid when the following condition is fulfilled:

$$\left| i\omega + \frac{1}{T_1} \left(1 - \frac{J(q + 2nQ)}{4k_B T} \right) \right| \gg \left| \frac{\beta S^2 J(q + 2nQ)}{2T_1} \right|.$$

This condition is satisfied for sufficiently large frequencies, which however still satisfy the condition to be smaller than the inverse high-temperature relaxation time T_1 as it is considered in this paper. At very low frequencies another approach should be used.

We have studied the dielectric susceptibility (10) behaviour using numerical constants appropriate to NaNO_2 . Between $T_c = 438.6$ K and $T_f = 437.4$ K there exists a stable modulated phase. The frequency dependence of the real and imaginary parts of the dielectric susceptibility calculated for both cases when the mode coupling is neglected (1) and when the mode coupling is taken into account (2) up to the fourth order in S is shown in figure 5 and figure 6.

There is a correction to the susceptibility in both cases. Note that a relatively pronounced correction is on the low-frequency side of the peak in $\text{Im } \chi$. The corrected value of $\text{Im } \chi$ of the susceptibility due to coupling is shifted above the uncorrected one. The contribution to $\text{Im } \chi$ of the susceptibility due to fourth-order terms leads to a higher absorption peak and an increase of this quantity in the low-frequency tail, see figure 6. Thus we see a clear tendency to create asymmetry of the peak present in the paraphase, namely on the low-frequency side.

In figure 7 the difference between $\text{Im } \chi$ calculated with and without coupling is displayed. We see that the coupling contribution has a peaklike shape and a tail to low frequencies. The peak maximum is at lower frequency than the peak maximum of $\text{Im } \chi$. This result is a basis for our expectation that the coupling to higher-order modes influences mainly the low-frequency dynamics.

The difference between the real part of the susceptibility $\text{Re } \chi$ calculated with and without coupling again displays changes that are most pronounced at low frequencies, where

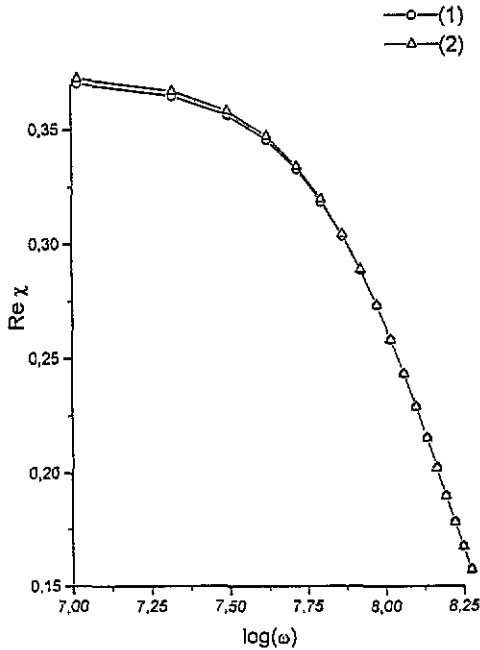


Figure 5. The frequency dependence of the real part of the dielectric susceptibility: (1) the mode coupling is neglected and (2) the mode coupling is taken into account up to the fourth order in S for NaNO_2 with $\delta = \frac{1}{8}$ and for temperature $T_f + 1 \text{ K} = 438.41 \text{ K}$.

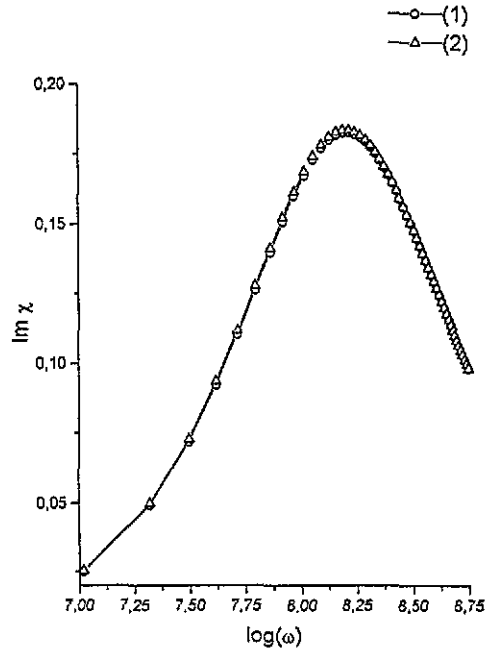


Figure 6. The frequency dependence of the imaginary part of the dielectric susceptibility: (1) the mode coupling is neglected and (2) the mode coupling is taken into account up to the fourth order in S for NaNO_2 with $\delta = \frac{1}{8}$ and for temperature $T_f + 1 \text{ K} = 438.41 \text{ K}$.

an increase is found when coupling is switched on. Near the peak frequency a small dip to negative values is found in both cases. At high frequencies the difference is vanishing.

From general time symmetry arguments it follows that we can define the effective relaxation frequency for any system, which may be expressed via the real and imaginary parts of the susceptibility transforming the susceptibility into the Debye-like form:

$$\chi = \frac{C(\omega)}{i\omega + 1/\tau(\omega)}.$$

Here the effective (real) relaxation time is

$$\frac{1}{\tau_{\text{eff}}(\omega)} = \frac{\omega\chi'}{\chi''}$$

and the effective (real) constant $C(\omega)$ can be expressed as

$$C(\omega) = \frac{\omega((\chi')^2 + (\chi'')^2)}{\chi''}.$$

In figure 8 the temperature dependence of the effective relaxation frequency τ_{eff}^{-1} is displayed for NaNO_2 for $\delta = \frac{1}{8}$ at low frequencies; the frequency corresponding to curve (1) is 2.5 times lower than the frequency corresponding to curve (2). The same frequency dependence was observed by Hatta [18, 19]. See also [17]. Mentioned measurements were made for a few different frequencies only. It would be desirable to perform systematic

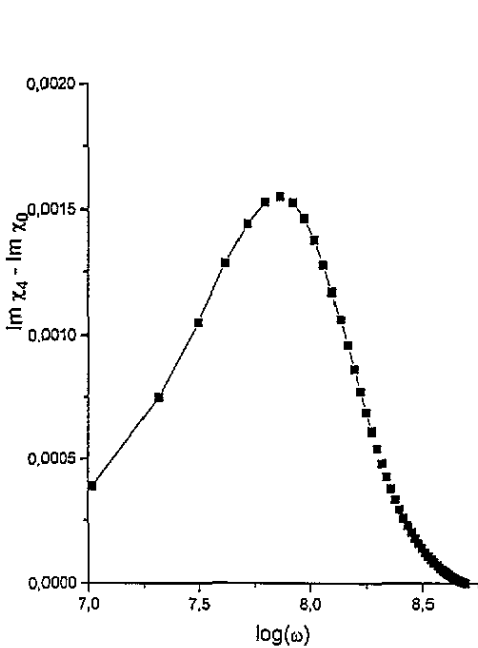


Figure 7. The difference between $\text{Im } \chi$ calculated with (subscript 4) and without (0) coupling is displayed: NaNO_2 with $\delta = \frac{1}{8}$ and for temperature $T_f + 1 \text{ K} = 438.41 \text{ K}$.

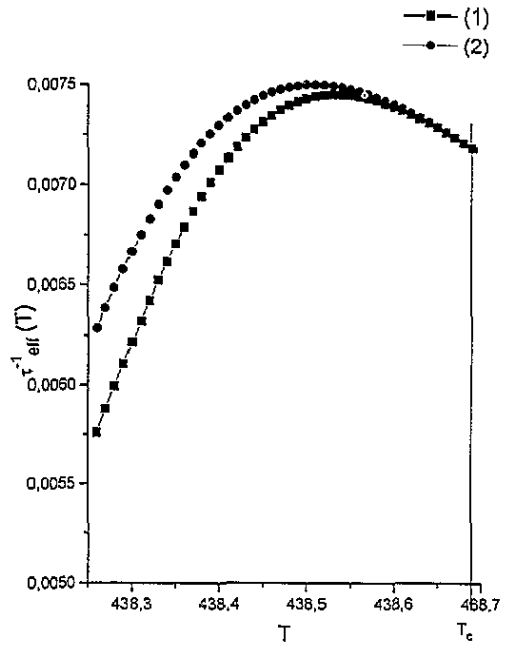


Figure 8. The temperature dependence of the effective relaxation frequency τ_{eff}^{-1} is displayed for NaNO_2 for $\delta = \frac{1}{8}$ at low frequencies: the frequency corresponding to curve (1) is 2.5 times lower than the frequency corresponding to curve (2).

measurements for more frequencies to understand how the temperature dependence of the relaxation time varies with frequency. This is the reason why we display the frequency dependence of the effective relaxation frequency τ_{eff}^{-1} in figure 9. It is interesting to display also the temperature (in figure 10) and frequency (in figure 11) dependences of the effective constant C .

The temperature and frequency dependences of the effective relaxation frequency and the frequency dependence of the effective constant C originate in the multirelaxation processes. Both quantities are frequency independent in the single-Debye-relaxation process. The incommensurate structures display complex frequency-dependent behaviour of both quantities due to the coupling between modes. Such a complex behaviour was observed in several dielectrics with incommensurate phases. While similar behaviour is observed also in glasses of the RADP type, their origin is more probably due to dynamics of defects and cluster walls, and not due to dynamics of frozen-in incommensurate regions. It is interesting that there exists a frequency region (see figures 8–11) between low-frequency and high-frequency behaviour. Above this region there are fast relaxation processes, while below it the relaxation processes are slower (the effective relaxation frequency is lower). The different behaviour may be explained by different relaxation times of processes which are effective above and below this region.

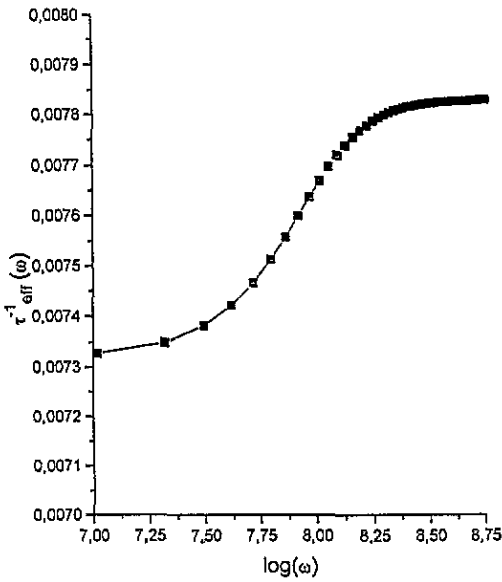


Figure 9. The frequency dependence of the effective relaxation τ_{eff}^{-1} is displayed for NaNO_2 for $\delta = \frac{1}{8}$ for temperature $T_f + 1 \text{ K} = 438.41 \text{ K}$.

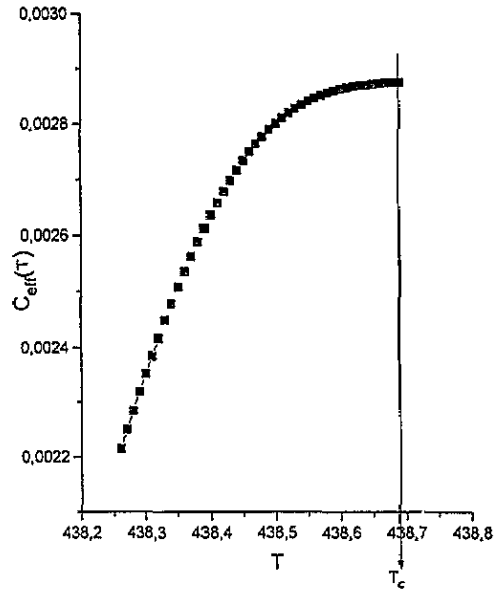


Figure 10. The temperature dependence of the effective C constant is displayed for NaNO_2 for $\delta = \frac{1}{8}$ at low frequencies: the frequency corresponds to curve (1) in figure 8.

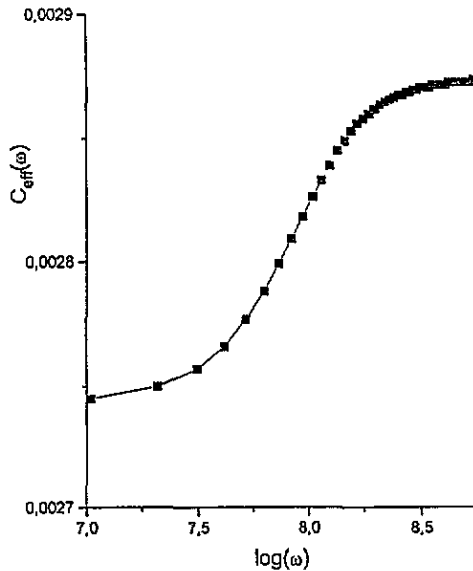


Figure 11. The frequency dependence of the effective C constant is displayed for NaNO_2 for $\delta = \frac{1}{8}$ at temperature $T_f + 1 \text{ K} = 438.41 \text{ K}$.

5. Discussion

5.1. General

Interactions of the uniform mode with higher-order modes due to the incommensurately modulated equilibrium state change the usual relaxation behaviour to a more complex

one. A multirelaxation character should be present even in the single-plane-wave limit. In this paper we took into account only several modes coupled to the basic uniform one. The incommensurate equilibrium state leads, however, to coupling of the uniform mode with an infinite number of modes. One may then expect that their contributions to the susceptibility will change substantially its behaviour. Thus the perturbation calculations used in previous section cannot give a satisfying description of the dynamics of this phase at lower temperatures and frequencies.

5.2. NaNO_2

Sodium nitrite crystallizes in the body-centred orthorhombic phase. Between $T_c = 438.6$ K and $T_f = 437.4$ K there exist a stable modulated phase [17]. The origin of this phase is a competition of the antiferroelectric coupling between the next-nearest neighbours and the ferroelectric coupling between the nearest neighbours. This is consistent with the study of interdipolar interactions performed by Yamada and Yamada [13]. The modulation wavevector was found to vary with temperature from $\frac{1}{8}$ at T_c to $\frac{1}{10}$ at T_f . There is no evidence of commensurate plateaux at simple rational values of the modulation wave vector. The orientational probability of the NO_2 dipoles can be described as a simple sine wave in the whole region of the modulated phase. The static dielectric susceptibility does not diverge at T_c due to ordering at the finite wave vector. It increases by more than one order of magnitude as $T \rightarrow T_c^+$. Deviation from the Curie–Weiss law is observed below 503 K. The dynamics of fluctuations is characterized by slow relaxational processes, there is no indication of a soft phonon mode. For a system of Ising spins close to its ordering temperature it is generally expected [17] that the dynamic order parameter susceptibility can be described in terms of a single Debye relaxation. Suzuki and Kubo [20] 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 was found in [21]. Hatta [18] verified the validity of the single-Debye-relaxation model above T_c . He was able to fit his measurements to

$$\tau_{\text{para}} = 2.4 \times 10^{-8} (T - T_0)^{-1.3} \text{ s.}$$

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 one expects two relaxation mechanisms with relaxation times corresponding to the amplitude and phase fluctuations. Both relaxation times are expected to be frequency independent [17]. An attempt to fit relaxation time to a single effective relaxation time leads to its frequency dependence. While the temperature behaviour of the effective relaxation time resembles that of the phase relaxations, according to the authors of [17] there is no reason why phase relaxation should dominate the dielectric response at $q = 0$ of the modulated structure. The frequency dependence of $\text{Im } \chi$ in the temperature region of the modulated phase shows clearly, see figure 1 in [18], a shift of the weight of $\text{Im } \chi$ with decreasing temperature to lower frequencies. As Hatta noted, below $T_c - 0.5$ the distribution of the relaxation times gradually broadens. Above this temperature a single-relaxation-time process takes place. Such a single-relaxation time picture would be consistent with the analysis of the Ising model dynamic susceptibility of Suzuki and Kubo [20], in which coupling of any given mode to other modes is neglected.

According to our qualitative results displayed mainly in figure 8–11, it is possible to interpret the temperature and frequency dependence of the effective relaxation frequency observed by Hatta [18], see also [17]. Indeed there is a correspondence between our theory and the results of the experiment: in the high-temperature region a single relaxation process

takes place, and the relaxational frequency is proportional to the temperature difference $T - T_0$; in the temperature region immediately below the transition temperature T_c a small local maximum in the temperature dependence of the effective relaxation frequency occurs; in the temperature region further below the transition temperature T_c a decrease of the effective relaxation frequency with decreasing temperature occurs; below the transition temperature T_c the effective relaxation frequency is frequency dependent: its value increases with increasing frequency. It would be of interest to perform a systematic experimental test of our theory, especially concerning the frequency dependence of the effective relaxation frequency.

5.3. Other systems

A simple lattice model with two sets of coupled Ising spins may explain many structural phase transitions including those in modulated $A'A''BX_4$ compounds [22]. In general one may expect that our discussion of the polydispersive processes applies to these systems too.

The relaxational time 5×10^{-10} s at 0.5 K above the incommensurate-ferroelectric phase transition in $RbH_3(SeO_3)_2$ has a typical value for order-disorder systems. The width of the distribution of relaxation times determined by the exponent β in Cole-Cole diagrams is found to be in the range $0.9 \leq \beta \leq 1$ within experimental accuracy $\delta\beta \simeq 0.1$ [23]. This may also indicate a slightly polydispersive behaviour.

The polydispersive dielectric process has been found also in the systems K_2SeO_4 and Rb_2ZnCl_4 , [24]. These materials are characterized by the relaxational frequencies of about 100 MHz at the incommensurate-ferroelectric phase transition temperature. The dielectric relaxation of both materials is described by a polydispersive process. Dielectric polydispersion is related, by the authors, to non-linear systems of discommensurations, where various kinds of mode are expected to be present. We note that such an intuitive picture is fully compatible with our model calculations. Thus these experimental results are in qualitative agreement with the results of our study although the systems are of the displacive type.

The monodispersive dielectric process of Debye type in the temperature range of the incommensurate phase except for the close vicinity of the incommensurate-commensurate transition was reported in $\{N(CH_3)_4\}_2ZnCl_4$, [25]. Again, however, two dispersions are present: above 1 MHz frequency range the Debye relaxation is observed and at low frequencies another one. The latter one becomes pronounced as temperature is lowered to T_c but the dispersion frequency is reported to be almost temperature independent. The former process is thought to be connected with the motion of discommensurations while the latter one is not (which was observed by means of the experiment on the signal field dependence). It is found that at temperatures between $T_c + 0.02$ K and $T_c + 0.5$ K the exponent β is within the range 0.8–0.92; at higher temperatures above $T_c + 0.5$ K a single relaxation time is found. The phase mode motion of discommensurations softens when the temperature approaches T_c . It would be interesting to perform experiments with the above-mentioned crystals in which the temperature and frequency dependence of the effective relaxational frequency was observed and to compare it with general expectations based on our theory.

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