Multirelaxational Dynamic Response In Incommensurate Phases.

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Abstract

Interactions of the uniform mode with higher order modes due to 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. Our model enables one to describe dynamic dielectric response of the incommensurable modulated phases in order-disorder systems.

1 Introduction

In this paper multirelaxational dynamic response in incommensurate phases is studied and extends results of our papers [1]-[5]. In [6] Lovesey et al. studied response of the incommensurate (INC) phase. They found that it may become very complex at low frequencies: there are quasi particle-like excitations and dispersion-less bands of excitations. The origin of such response is in the fragmentation of the excitation energy spectrum. It occurs in magnetic materials, linear chains of atoms, electrons in the perpendicular magnetic field on lattice. In the incommensurate phase it is found that response exists at very low frequencies $\omega \to 0$ in spite of presence of strong site anisotropy.

In the ferroelectric material with an INC phase and dielectric relaxation (NaNO$_2$ which has body-centered orthorhombic phase there is between $T_c = 438.6K$ and $T_f = 437.4K$: a stable modulated phase. The modulation wave-vector varies with T from $\frac{1}{8}$ at $T_c$ to $\frac{1}{10}$ at $T_f$ decreasing temperature. There is no evidence of commensurate plateaux. Orientational probability of the NO$_2$
dipoles leads to a simple sine wave in the whole region of the modulated phase. Below $T_c$ one expects two relaxation mechanisms with frequency independent relaxation times corresponding to the amplitude and phase fluctuations, see in [7].

For a system of Ising spins close but above $T_c$ the order parameter dynamic susceptibility has a single Debye relaxation

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

A monodispersive dielectric relaxation in the paraelectric phase in $NaNO_2$ is found found by Hatta [8]. The Cole-Cole diagram gives $\beta = 0.94$ in the single Debye relaxation process. Hatta verified the validity of the single Debye-relaxation model above $T_c$:

$$
\tau_{para} = 2.4x10^{-8}(T - T_0)^{-1.3}s.
$$

$T_0$ is the same as found from the fit of the static susceptibility above $T_c$ to the Curie-Weiss law. Below $T_c$ an attempt to fit 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 relaxations there is no reason why phase relaxation should dominate the dielectric response at $q = 0$ of the modulated structure. The frequency dependence of $Im\chi$ in the temperature region of the modulated phase shows clearly a shift of the weight of $Im\chi$ with decreasing temperature to lower frequencies. As Hatta noted below $T_c - 0.5$ the distribution of the relaxation times gradually broadens.

In $RbH_3(SeO_3)_2$ there exists the incommensurate-ferroelectric phase transition. The Cole-Cole diagram gives:

$$
0.9 \leq \beta \leq 1
$$

with experimental accuracy $\delta\beta \simeq 0.1$, see in [9]. This may indicate a slightly polydispersive behaviour.

In $K_2SeO_4$ and $Rb_2ZnCl_4$ the polydispersive dielectric process has been found [10]. Note that in $Rb_2ZnCl_4$ the Cole-Cole diagram shows additional dispersive process increasing its contribution at lower frequencies (about 22 MHz) and lower temperatures (in $K_2SeO_4$ it is so about 5 MHz). The dielectric polydispersion is related by the authors to non-linear systems having discommensurations where various kinds of modes are expected to be considered.

In $\{N(CH_3)_4\}_2ZnCl_4$ [11] the monodispersive dielectric process of the Debye type is observed in the incommensurate phase except for close vicinity of the incommensurate-commensurate transition $T_c + 0.02K - T_c + 0.5K$ where $\beta$ is within $0.8 - 0.92$. However above $T_c + 0.5K$ a single relaxation time is found. There are two additional dispersions: above 1 MHz frequency range the Debye relaxation is observed and at low frequencies another one. The latter one is pronounced as temperature is lowered to $T_c$ but the dispersion frequency is almost temperature independent. The former process is thought to be connected with the motion of discommensurations while the latter one is not (observed by means of the signal field dependence).

In $Rb_2ZnBr_4$ the incommensurate phase has unusual temperature independence of the modulation wavevector [12]-[14]. Its behaviour is inconsistent with
the commonly accepted point of view: $T$ dependence of the real part of the dielectric tensor is due to increasing distance between discommensurations, as f.e. in $K_2SeO_4$. In $(NH_4)_2BeF_4$ the polydispersive processes are present in the incommensurate phase [15]. The complex dielectric constant of $(NH_4)_2BeF_4$ single crystals was measured in the frequency range from 0.6 to 300 MHz in the vicinity of the transition temperature, the relaxation frequency is about 108 Hz at $T_c$. This is the order-disorder type system and its Cole-Cole diagram gives Debye type polydispersion with the coefficient $\beta = 0.7$. In the lower frequency range below 6 MHz: the additional low frequency dispersion process is present relaxation time of which exceeds that for the "domain like structure".

In $RbH_3(SeO_3)_{2}$ the relaxation time $5 \times 10^{-10}$ s at 0.5$^\circ$ above the incommensurate-ferroelectric phase transition temperature is present, which is typical for order-disorder systems. $\beta$ in Cole-Cole diagrams is:

$$0.9 \leq \beta \leq 1$$

within experimental accuracy $\delta \beta \simeq 0.1$ [16]. According to the authors: this is nearly monodispersive character; to be due to discommensurations.

In general in $A'AA'BX_4$ compounds a simple lattice model with Ising spins is a basis for qualitative discussions of relaxation phenomena in many structural phase transitions including displacive modulated [17]. Then one may expect that discussion of the polydispersive processes in order-disorder materials may become relevant in general also to these systems.

Interactions in these materials are of the type: homogeneous mode - higher order modes due to incommensurate modulated ground state, does this fact change usual relaxation behaviour to more complicated? Is in this case a multirelaxation response present even in the single plane wave limit? Should be domain-like structures in incommensurate dielectrics near the lock-in transition to the lower ferroelectric phase responsible for distribution of the relaxation times in the incommensurate structures? How to increase the number of types of materials in which the fragmentation of the excitation energy spectrum may be confronted with reality?

Main results of this paper are: The complex dynamical susceptibility was calculated using the Bloch equations. Perturbation and nonperturbation approach enabled us to derive formulae for susceptibility which display multirelaxational behaviour due to the coupling of the homogeneous polar soft mode to higher-order modes. We obtained results of numerical studies of multirelaxation phenomena due to interaction of modes and their comparison with experimental behaviour in some dielectric materials. We introduced an approximative model which gives explicitly nonperturbation results. At the of the paper there is a discussion.

## 2 Model

A model Hamiltonian $H_T$ which we will use is well known (description in f.e. [18]. A similar model is used in the description of modulated structures in magnetism [19]-[25] and in in dielectrics ( $NaNO_2$ ) [26], and in the ANNNI model (i.e.
Here $S^z_i$ are pseudospin variables $S^z_i = \pm \frac{1}{2}$, we assume a simple cubic lattice $i = 1, \ldots, N_{\text{latt}}$, where $N_{\text{latt}}$ is the number of sites, each site is a fluctuating unit (e.g., H, D, NO$_2$). In real materials (KDP, NaNO$_2$ type, etc.) there are more complicated structures which need for description more complex models.

We use for simplicity:

$Q \equiv Q \cdot a$,

where $a$ is a basic lattice vector $(1,0,0)$. The interaction energy $J(q)$ for $q$ in the $a$ direction is given by:

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

The random-phase-approximation type analysis gives:

$$\langle S^z_n \rangle = \frac{1}{2} \tanh(\beta \frac{H_n}{2}),$$

$$H_n = \sum_j J_{nj} \langle S^z_j \rangle,$$

and $kT_c = \frac{J(Q)}{4J_{\text{perp}}}$ defines the transition temperature $T_c$. The single plane wave modulated state is given by:

$$\langle S^z_n \rangle = S \cos(Qn + \phi).$$

Here $\phi$ is an arbitrary phase and the local field on the site $n$ is:

$$H_n = SJ(Q) \cos(Qn + \phi).$$

The modulation vector amplitude is:

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

Note that $Q$ is incommensurate if it is different from the number $2\pi \frac{M}{N}$, where $M, N$ are any integers.

In real materials we have: for DRADP: $\frac{Q}{2\pi} \approx 0.35$, for $Rb_2ZnBr_4$: $\frac{Q}{2\pi} \approx \frac{5}{17}$, for $NaNO_2$: $\frac{Q}{2\pi} \approx \frac{1}{3}$ immediately below $T_c$.

The equilibrium state energy:

$$E_{\text{GS}} = -N_{\text{latt}}J(Q)\frac{S^2}{2},$$

for small amplitude of the basic harmonics, $S$, given by:

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

Numerical values of model constants for $NaNO_2$ are: $J_1 \approx 81K$, $J_2 \approx -26K$, $J_{\text{perp}} \approx 410K$, $T_c = 438.69K$. The Curie-Weiss temperature for the
direct para-ferroelectric (virtual) transition is \( T_0 = 437.41K \), here the virtual transition temperature is \( kT_0 = \frac{437}{1.38} \). However the transition temperature for the incommensurate to ferroelectric phase transition is 436.24 K. The phase above the incommensurate one is the paraphase.

The high temperature relaxation time constant estimated is estimated to be \( T_1 = 0.7922K^{-1} \). The incommensurate parameter is \( \delta = \frac{1}{8} \).

The small amplitude approximation in (5) as restricted to temperatures not very low with respect to the transition temperature is:

\[
S^2 \approx (1 - \frac{T}{T_c}).
\]

Let us assume that Q is a modulation vector amplitude in the incommensurate single plane wave modulated phase. The dynamics of excitations using Bloch equations for the motion of pseudospins [1] may be described by the method well known and thoroughly discussed in [18] in which the equations of motion for pseudospins is:

\[
i\omega \delta < S_i^z > = -\frac{1}{T_1} \delta < S_i^z > - \frac{\beta}{4}(1 - 4 < S_i^z >^2).
\]

\[
\sum_j J_{ij} \delta < S_j^z > - \frac{\beta}{2}(1 - 4 < S_i^z >^2) \mu E_i]
\]

where \( \delta < S_i^z > \) is mean values of amplitudes of fluctuating pseudospin at site i

\[
< S_i^z > = < S_i^z > + \delta < S_i^z > \exp(i\omega t),
\]

here \( \mu \) is the dipole moment of the elementary unit, \( T_1 \) is the longitudinal high-temperature relaxation time, the molecular field \( H_i \), at site i:

\[
H_i = (0, 0, \sum_j J_{ij} < S_j^z >) = (0, 0, H_i).
\]

If a general time and site dependent electric field \( E_i(t) \) is applied to the equilibrium state (2) then an infinite set of equations (the Fourier transform of (6)) is given by:

\[
a_n S_n + b_{n-1} S_{n-1} + b_{n+1} S_{n+1} = c e_n + g e_{n-1} + g e_{n+1},
\]

where \( n \) is integer, here \( \beta = \frac{4\pi T}{k_B T_c} \), and

\[
a_n = (i\omega + \frac{1}{T_1} - \frac{\beta J(q + 2nQ)}{4T_1}(1 - 2S^2)) \]

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

\[
c = \frac{\beta \mu}{2T_1}(1 - 2S^2)
\]

\[
g = \frac{\beta \mu S^2}{2T_1}
\]

\[
E_n = E_{q+2nQ}
\]

\[
e_n = E_n \exp(-i2\phi n)
\]

\[
S_n = \delta < S_{q+2nQ} > \exp(-i2\phi n).
\]
Note that the homogeneous field is coupled to an infinity set of modes in the incommensurate state.

The case of a commensurate phase: a periodicity in the n variable is found and a finite number of quasiparticle bands. The incommensurate case fluctuation spectrum is complex in the exact mathematical sense - a well known Cantor set of points in the energy spectrum.

3 Paraphase

In the paraphase the susceptibility can be calculated from:

\[ \chi = \frac{2\mu \sum \delta < S_i^2 >}{N_{tot} E} \]

in a homogeneous electric field with amplitude E. We obtain:

\[ \chi_{para} = \frac{\mu^2}{i\omega + \frac{1}{T_1} (1 - \frac{J(0)}{T})}. \] \hspace{1cm} (10)

Here we find the Debye relaxation type behaviour:

\[ \frac{1}{T_1} (1 - \frac{T_0}{T_c}) \]

at \( T_c \).

where for \( NaNO_2 \) \( J(O) > 0 \), this behaviour observed by Hatta [28]-[29].

4 Incommensurate phase

Below \( T_c \), the transition temperature to the incommensurate phase, S is the perturbation parameter we calculate when neglecting coupling of the \( q = 0 \) mode to other modes (would be absent in the uniform equilibrium state). Then the dielectric susceptibility:

\[ \chi_{INC} = \frac{\mu^2 (1 - 2S^2)}{i\omega + \frac{1}{T_1} (1 - 2S^2)}. \] \hspace{1cm} (11)

We find the Debye-relaxation type dispersion, the C constant in \( \chi_{INC} \) is modified with respect to its paraphase value by the factor \( (1 - 2S^2) \). Note: for the uniform phase (with \( Q=0 \)) \( 2 \) in this factor should be replaced by \( 4 \).

If modulation wave vector Q is commensurate then a finite number of modes \( S_0, \pm 1, ... \) would contribute to the susceptibility. If Q is incommensurate theoretically all higher order terms will contribute to the susceptibility. For the dielectric susceptibility of the incommensurate phase up to the fourth order in S we find:

\[ \frac{\chi^4}{2\mu} = \frac{\chi_{para}^2}{2\mu} - S^2 \left( \frac{c_1}{\alpha_0^2} + \frac{c_2}{\alpha_0^4} \right) + S^4 \left( \frac{c_{06}^2}{\alpha_0^6} \right) - \frac{gb}{\alpha_0^2 \alpha_1} - \frac{gb - 1}{\alpha_0^2 \alpha_{-1}} + \frac{c_{06} b_1}{\alpha_0^2 \alpha_1} + \frac{c_{06} b_{-1}}{\alpha_0^2 \alpha_{-1}} + O(S^6), \] \hspace{1cm} (12)
where

\[ \alpha_n = \left( i\omega + \frac{1}{T_1} - \frac{\beta J(q + 2nQ)}{4T_1} \right) \]

\[ \beta_n = \frac{\beta J(q + 2nQ)}{2T_1} \]

\[ a_n = \alpha_n + S^2\beta_n \]

\[ c_0 = \frac{\beta \mu}{2T_1} \]

\[ c_1 = \frac{\beta \mu}{T_1} \]

\[ c = c_0 - c_1 S^2. \]

(13)

The expansion in powers of \( S^2 \) is valid when the following condition is fulfilled

\[ | i\omega + \frac{1}{T_1} (1 - \frac{J(q + 2nQ)}{4k_BT}) | >> | \frac{\beta S^2 J(q + 2nQ)}{2T_1} |. \]

This condition is satisfied for sufficiently large frequencies, which are still smaller than \( T_1 \). At very low frequencies another approach should be used.

The frequency dependence of the real and imaginary part 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 \( S \). The contribution to \( Im\chi \) due to fourth order terms gives higher absorption peak, an increase of this quantity in the low frequency tail, tendency to create asymmetry of the peak present in the paraphase on the low frequency side.

The difference between \( Im\chi \) calculated with and without coupling is in the fact that the coupling contribution has a peak-like shape and a tail to low frequencies. The peak maximum is at lower frequency than the peak maximum of \( Im\chi \).

The difference between the real part of the susceptibility \( Re\chi \) calculated with and without coupling gives that changes are most pronounced at low frequencies.

Let us note that general time symmetry arguments gives that real and imaginary part of the susceptibility into the Debye-like form:

\[ \chi = \frac{C(\omega)}{i\omega + \frac{1}{\tau(\omega)}}. \]

the effective (real) relaxation time

\[ \frac{1}{\tau_{eff}(\omega)} = \frac{\omega \chi'}{\chi''}. \]

the effective (real) constant \( C(\omega) \)

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

There is a temperature dependence of the effective relaxation frequency \( \tau_{eff}^{-1} \) for \( NaNO_2 \) for \( \delta = \frac{1}{3} \) at low frequencies. Frequency corresponding to the curve (1) is 2.5 times lower than the frequency corresponding to the curve (2).
The same frequency dependence was observed by Hatta (above) and discussed in [7]. Note that existing measurements are done for a few different frequencies only. Desirable is to perform systematic measurements for more frequencies to understand how temperature dependence of the relaxation time varies with frequency, frequency dependence of the effective relaxation frequency \( \tau_{eff}^{-1} \), temperature and frequency dependence of the effective constant C, temperature and frequency dependence of the effective relaxation frequency and frequency dependence of the effective constant C originate in the multirelaxation processes. Both quantities are frequency independent in the single Debye relaxation process. Between low frequency and high frequency we find that above there are fast relaxation processes, and below there are relaxation processes slower (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. Expectation that the coupling between the homogeneous mode and higher order modes influences mainly the low frequency dynamics should be verified by nonperturbation calculations.

5 Mode-independent approximations

Purpose of this section is to introduce several approximations within previously defined model, which enable to study equations (9) in a mathematically closed form. We find that the solution is physically non-trivial, displays new features concerning multirelaxational response of incommensurable modulated phases.

The paraphase - ferrophase phase transition usually is splitted into at least two transitions: paraphase - incommensurate phase and incommensurate phase - ferrophase. INC phase temperature region is small near virtual phase transition paraphase - ferrophase temperature.

The interaction energy \( J(q) \) has a maximum value at \( q=Q \) - modulated state, and a minimum value at \( q=0 \) - ferroelectric state (\( NaNO_2 \))

\[
\delta \equiv \frac{J(Q) - J(0)}{J(0)} = \frac{T_c - T_0}{T_0}.
\]

Consider systems in which (max) value of \( J(Q) \) is only slightly higher than lowest \( J(0) \) value. Estimate for \( NaNO_2 \) gives 0.005.

\( J(q) \) for any but \( q=Q \) is approximated in the zero order in \( \frac{T_c - T_0}{T_0} \) by:

\[
J(q) \approx J(0) + \frac{J(Q) - J(0)}{2}(\delta_{q,Q} + \delta_{q,-Q}).
\]

Note: this approximation gives simplified dynamic equations. \( J(q) \) in direct space has the form:

\[
J(r - m) = J(0)\delta_{r,m} + (J(Q) - J(0))\cos(Q(r - m)).
\]

\( J(r) \) is infinity-range effective oscillatory pseudospin-pseudospin interaction energy. Single wave ground state remains still sinusoidally modulated with \( q=Q \). Now we have:

\[
J(2nQ) = J(0)
\]

for all non-zero integers n if Q takes an incommensurate value. Thus we assume: for those values of the system parameters, for which the quantity in (14)
is small, the incommensurate phase may be practically characterized by the single plane wave regime. We neglect quantities of the order $T_c - T_0$ and higher, while we still consider fluctuations $S_n$ of the order $S^{2n}$. It is clear that our approach is more correct for temperatures nearby the transition from paraphase to incommensurate phase.

Mode-independent approximation gives mode independent relaxation time:

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

an effective interaction energy $J(0)$ leads to a single relaxation frequency

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

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

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

which is a mode (index n) independent form.

Physics in this approximation is that an original set of different relaxation times is represented by the largest one. Mode independent relaxation energy approximation gives in (9) a set of interaction constants

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

for different modes of fluctuations. An effective interaction energy $J(0)$:

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

which is mode (index n) independent form.

An approximation for the dynamic equations assuming mode independent approximation to the equations (9) is:

$$(i\omega + a)S_n^0 + bS_{n-1}^0 + bS_{n+1}^0 = ce_n + ge_{n-1} + ge_{n+1}. \quad (15)$$

Here $\delta a_n = a_n - a$, $\delta b_n = b_n - b$, $\delta S_n = S_n - S_n^0$. $S_n$ is assumed to satisfy (9). (15) is equivalent to the original equations (9) if we simultaneously solve also:

$$a_n\delta S_n + b_{n-1}\delta S_{n-1} + b_{n+1}\delta S_{n+1} = -\delta a_nS_n^0 - b_{n-1}S_{n-1}^0 - b_{n+1}S_{n+1}^0. \quad (16)$$

Thus our approximation to reduce (9) to (15) is the same as to (16) with respect to (15). Further we discuss only (15).

An approach to incommensurability via a limiting process using a sequence of commensurate phases: the infinite set (15) easily solved using limiting procedure: the incommensurate phase with the modulation wavevector $Q$ is approached by a sequence of commensurate phases with the modulation wavevectors $Q(L,M)$

$$Q(L, M) \equiv \frac{2\pi M}{L},$$
where
\[ \lim_{M,L \to \infty} Q(L, M) = Q. \]

Steps in the procedure are: a procedure which leads to solution of (9) consists of solution of (15) for finite appropriate \( L \) and \( M \) integers, and then taking the limit above.

A solution for a general mode is, assuming that \( Q \) is commensurate (\( M \) and \( L \)), in the form
\[ S_n = \sum_{\kappa} \exp \left( i \frac{2\pi}{L} \kappa n \right) S_\kappa, \]
for any value of momentum \( q \). Note that the periodicity condition holds \( S_{n+L} = S_n \). From (15) we obtain
\[ S_\kappa = \frac{1}{L} \sum_n \frac{(c + g e_n - 1 + g e_{n+1}) \exp \left( -i \frac{2\pi}{L} \kappa n \right)}{i\omega + a + 2b \cos \left( \frac{2\pi \kappa}{L} \right)} + 2 \]

The inverse form, the homogeneous field has the form:
\[ S_n = \frac{1}{L} \sum_{\kappa} \frac{(c + 2g \cos \left( \frac{2\pi \kappa}{L} \right)) \exp \left( i \frac{2\pi}{L} \kappa n \right)}{i\omega + a + 2b \cos \left( \frac{2\pi \kappa}{L} \right)}, \] (17)
which is a general form for the motion of the \( n \)-th mode due to the external field.

### 6 Dynamic susceptibility

Dynamic dielectric susceptibility \( \chi \) taking appropriate limit to \( Q \) is given by:
\[ \chi = \frac{\mu N_{\text{lat}}}{\pi} \int_{-\pi}^{+\pi} \frac{(c + 2g \cos(x))}{i\omega + a + 2b \cos(x)} \, dx. \] (18)

The real part of the susceptibility is:
\[ \chi' = \frac{\mu N_{\text{lat}}}{\pi} \int_{-\pi}^{+\pi} (a + 2b \cos(x))(c + 2g \cos(x)) \, \frac{\omega^2 + (a + 2b \cos(x))^2}{dx}. \] (19)

The imaginary part of susceptibility is:
\[ \chi'' = -\frac{\omega \mu N_{\text{lat}}}{\pi} \int_{-\pi}^{+\pi} (c + 2g \cos(x)) \, \frac{\omega^2 + (a + 2b \cos(x))^2}{dx}. \] (20)

### 7 Static susceptibility

The zero-frequency limit of (18) is the static susceptibility \( \chi_0 \):
\[ \chi_0 = \frac{\mu^2 N_l}{k_B T} \frac{1}{\sqrt{\frac{T - T_0}{T} + \frac{4\mu^2 \kappa}{T}}} \] (21)
\[1 - 2S^2 - \frac{T}{T_0}\left(\sqrt{\frac{T - T_0}{T}} + \frac{4S^2T_0}{T} + \frac{T - T_0}{T_0}\right) - (1 - \frac{T}{T_0}(1 - 2S^2)) \].

Decreasing temperature, above \(T_c\), behaviour is of the mean field type:

\[\chi_0 \approx \frac{1}{T - T_0}.\]

The critical index in this temperature region is 1. Decreasing further temperature below \(T_c\), but still above \(T_0\) gives that the critical behaviour of the static susceptibility changes to

\[\chi_0 \approx \frac{1}{\sqrt{T - T_0}}\]

and the critical index changes to \(\frac{1}{2}\). Our model predicts different critical behaviour for the static susceptibility in the modulated region. The behaviour of the inverse static susceptibility (21) has a local minimum around \(T_c\) which is then changed to a local maximum followed by a steep decrease. This may describe uncertainty as concerning the experimental behaviour of the dielectric static susceptibility, see in [7] where the values of the critical index is reported as 1.11-1.24. Those values are obtained from fits within the paramagnetic phase, where dielectric static susceptibility displays departure from the mean field behaviour, which occurs above 500 K only. Thus there is a question: Do interacting fluctuations of the forming incommensurate phase renormalise paraaphase behaviour in the way corresponding to experiments? Do our results indicate such possibility?

8 Dispersion-less modes

The response of the incommensurate structure consists of a sum of infinite number of relaxators with their relaxation frequencies:

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

After substitution of a and b constants we obtain:

\[\frac{1}{\tau_x} = \frac{T - T_0}{T_1T} + \frac{T_0S^2\cos^2(\frac{x}{2})}{T_1T}\]

The effective temperature \(T_0\) is defined as

\[\frac{J_0}{4k_B}\]

The maximum of the relaxational frequency is:

\[\frac{T - (1 - S^2T_0)}{T_1T}\]

and the minimum of the relaxational frequency is:

\[\frac{T - T_0}{T_1T}.\]
Both extremal values are the same when the temperature increases to the transition temperature $T_c$. Their difference reveal such a behaviour explicitly:

$$\max \frac{1}{\tau_{eff}(x)} - \min \frac{1}{\tau_{eff}(x)} = \frac{S^2 T_0}{T_1 T}.$$  
Thus: spread of relaxational frequencies increases decreasing temperature below the transition temperature. The Curie constants are:

$$\mu N_{latt} \frac{c + 2g \cos(x)}{\pi} \left( \frac{a + 2b \cos(x)}{2} \right).$$

Both quantities, relaxation frequency and Curie constant, are mode dependent, see their x-dependence.

Another form of the dynamic susceptibility is:

$$\chi = \chi_0 \int_{-\pi}^{+\pi} \frac{w(x)}{i\omega \tau_x + 1} dx,$$  
(22)

here $\chi_0$ is the static susceptibility, the weight of an x-relaxation mode contribution to the susceptibility is:

$$w(x) \equiv \frac{1}{2\pi \chi_0} \frac{1 + 2S \cos(x)}{1 + 2b \cos(x)}. $$

The weight is normalized to unity:

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

The explicit form of the weight function is:

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

Below the critical temperature and above the effective temperature $T_0$ there exists no singular point in the weight function. Interpretation of the form (22) is: susceptibility = the sum of an infinite number of relaxation modes, each characterized by the label x, its density $w(x)$, and its relaxation frequency $1/\tau_x$.

These modes contribute at the same frequency $\omega$. We have found continuum of states of excitations characterized by the continuously varying weight $w(x)$ instead of the quasiparticle-like spectrum (the weight function of which consisting of a sum of singular delta terms). An interpretation of excitation spectra within our model is closely related to that for other systems made by Lovesey and his coworkers [22] and [25]. Lovesey’s approach usually predicts also existence of nonzero density of states at zero frequency, our approach gives the quantity $y_- > 0$ as the lowest frequency of these excitations.

### 9 Dielectric losses

The imaginary part of the dynamic susceptibility as transformed is:

$$\chi'' = \frac{\chi_0 e^{-\omega}}{\pi} \int_{y_-}^{e^{\omega}} dy \frac{1}{\sqrt{y_+ - y)(y - y_-)} \left( 1 + \frac{2g \delta_-}{y^2 + \omega^2} \right)$$  
(23)
where

\[ \chi_0 \equiv 2\mu N_{\text{lat}} \frac{c}{a}, \]

\[ \delta_{\pm} \equiv y_+ \pm y_- . \]

Here \( y = a + 2b \cos(x) \). From (23): the weight \( w(y) \) is proportional to the inverse square roots:

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

The first root has singularity at the point \( y_+ \):

\[ y_+ = \frac{1}{T_1}(1 - \frac{\beta J(0)}{4k_B}(1 - 4S^2)) . \]

Note: it does not depend on temperature if we use:

\[ S^2 = \frac{1}{4}(1 - \frac{T}{T_c}) \]

instead of the original simplified one:

\[ S^2 = (1 - \frac{T}{T_c}) . \]

Then \( y_+ \) takes the form:

\[ y_+ = \frac{1}{T_1}(1 - \frac{T_0}{T_c}) . \]

The explicit form of the lower root singularity is:

\[ y_- = \frac{1}{T_1}(1 - \frac{T_0}{T}) . \]

Note: both quantities, \( y_{\pm} \) are positive for temperatures higher than \( T_0 \). Decreasing temperature towards \( T_0 \) the quantity \( y_- \) vanishes and lower and lower relaxation frequencies become active. Real transition temperature from the incommensurate to the ferroelectric phase is slightly higher than temperature \( T_0 \). The weight of low frequency relaxation movements of pseudospins increases decreasing temperature.

10  Real part of the susceptibility

The real part of the dielectric susceptibility is easily transformed to the more instructive form:

\[ \chi' = \frac{\chi_0}{\pi} \int_{y_-}^{y_+} dy \frac{y}{\sqrt{(y_+ - y)(y - y_-)}} \frac{1 + \frac{2g(2y - \delta_+)}{\delta_-}}{y^2 + \omega^2} . \]  (24)

interpretation of which is easy.
11 Frequency behaviour

Low frequency behaviour for temperatures $T > T_0$ is the following. Note that for $T > T_0$ we have $y_- > 0$ and the low frequency here is defined by the condition:

$$\omega < y_-.$$  

From (23) and (24) we obtain approximative expressions for real and imaginary dielectric susceptibilities:

$$\chi' \approx A - B\omega^2 + O(\omega^4)$$

and

$$\chi'' \approx C\omega - D\omega^3 + O(\omega^5).$$

Here we have found that:

$$a \equiv 1 - \frac{2g}{c} \frac{y_+ + y_-}{y_+ - y_-}$$

$$b \equiv \frac{1}{c} \frac{y_+ - y_-}{y_+ - y_-}$$

$$A = I_2 a + I_1 b$$

$$B = I_4 a + I_3 b$$

$$C = I_1 a + I_0 b$$

$$D = I_3 a + I_2 b$$

$$I_0 = 1$$

$$I_1 = \frac{1}{\sqrt{y_+ y_-}}$$

$$I_2 = \frac{y_+ + y_-}{2(y_+ y_-)^2}$$

$$I_3 = \frac{3(y_+ + y_-)^2 - 4y_+ y_-}{8(y_+ y_-)^2}$$

$$I_4 = \frac{15(y_+ + y_-)^3 - 36y_+ y_-(y_+ + y_-)}{48(y_+ y_-)^2}.$$  

Maximal losses are at the frequency:

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

The halfwidth of this peak is:

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

The effective relaxational frequency becomes frequency dependent:

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

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where \[ \frac{1}{\tau_{\text{eff}}(0)} \equiv \frac{A}{C} \] and \[ \rho \equiv \frac{B}{A} - \frac{D}{C}. \]

The effective relaxational frequency quadratically increases when frequency increases, at least at low frequencies and for temperatures immediately below the transition temperature.

Calculating approx. constants A,B,C and D we obtain:

\[
\frac{1}{\tau_{\text{eff}}} \approx \frac{1}{\tau_{\text{eff}}(0)} \left(1 + \alpha(\omega^2 \tau_{\text{eff}}^2(0))S^4\right). \tag{25}
\]

The correction to zero-frequency behaviour is of the order $S^4$ in agreement with our previous perturbation calculations. Zero frequency effective relaxational frequency $\frac{1}{\tau_{\text{eff}}(0)}$ is temperature dependent:

\[
\frac{1}{\tau_{\text{eff}}(0)} = \frac{1}{T_1} \sqrt{\frac{\alpha^2 - 4b^2}{\alpha^2 - 4b^2 - T_1}}
\]

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 effective zero-frequency relaxation frequency below transition temperature from paraphase to the incommensurate phase is:

\[
\frac{1}{T_1} \frac{\beta J(0)}{4T_1}.
\]

At the transition point both quantities are continuously connecting each other:

\[
\frac{1}{\tau_{\text{eff}}(0)} \approx \alpha \approx (T - T_0),
\]

below this temperature point fluctuations renormalise the temperature dependence

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

Softening of the relaxational frequency below $T_c$ continues from above this point, however proportionality coefficient is renormalized.

Experiments by Hatta (1970) [9] for $NaNO_2$ reveal that immediately below the transition to the incommensurate phase frequency dependence of the effective relaxation frequency, behaviour found within this theory corresponds qualitatively with that observed by Hatta: increasing frequency relaxational frequency increases too. Also temperature dependence qualitatively corresponds to observed. More precise comparison of our predictions with experiments is desirable and not only for $NaNO_2$ materials.
High frequency behaviour for temperatures $T > T_0$ has $y_+ > 0$, which remains finite for considered temperature region. The high frequency region is defined by the condition:

$$\omega > y_+.$$ 

Both parts of the susceptibility have approximate frequency behaviour:

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

and

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

Here $F$ and $G$ are temperature dependent constants. Both parts of the susceptibility vanish in power-like way increasing frequency. Qualitatively such behaviour resembles behaviour of a single Debye-like relaxator. The effective relaxational frequency becomes frequency independent:

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

Intermediate frequency behaviour for temperatures $T > T_0$, where the intermediate frequency is defined by the condition:

$$y_- < \omega < y_+,$$

gives below the transition from para to incommensurate phase that the intermediate frequency region is very small, decreasing temperature its range increases. When the inequality above holds, then both parts of the susceptibility cannot be expanded directly in powers of frequency.

12 Discussion

Let us first discuss our results for NaNO$_2$ and then for other systems.

12.1 NaNO$_2$

Within our results it is qualitatively possible to interpret temperature and frequency dependence of the effective relaxation frequency observed by Hatta. In high temperature region a single relaxation process takes place, and the relaxational frequency is proportional to temperature difference $T - T_0$. In the temperature region immediately below the transition temperature $T_c$ a small local maximum in 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.
12.2 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. In general one may expect that our discussion of the polydispersive processes applies to these systems too. The polydisperse dielectric processes in $K_2ScO_4$ and $Rb_2ZnCl_4$ are related by some authors to non-linear systems of discommensurations, where various kinds of modes are expected to be present. Note: such an intuitive picture is compatible with our model calculations. In $\{N(CH_3)\}_2ZnCl_4$ it would be interesting to perform experiments with these mentioned crystals in which temperature and frequency dependence of the effective relaxational frequency was observed and to compare it with general expectations based on our theory. While similar behaviour is observed also in the glasses of the RADP type, their origin is more probable due to dynamics of defects and cluster walls, and not due to dynamics of frozen-in incommensurate regions.

13 Conclusions

Interactions of the uniform mode with higher order modes due to 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. Our model enables one to describe response of the incommensurable modulated phases in order-disorder systems: while more detailed mathematical approach would predict known Cantor set type of the fragmented energy spectrum, it would be difficult to verify such spectrum and its consequences in real materials. Our approach is based on the idea of envelope description of this energy spectrum and as such it certainly omits some specific to Cantor sets points of view. On the other hand approximations used here are still of the predictive value: there are qualitatively new predictions concerning response of the incommensurate phase in order-disorder type of systems.

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