NMR Relaxation in Incommensurate Systems with a Double q Modulation

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The NMR lineshape and relaxation rates are evaluated for a superposition of two incommensurate modulation waves with an arbitrary ratio of modulation wave vectors $|\vec{q}_1|/|\vec{q}_2|$ and an arbitrary angle between the two modulation directions.

Phase transitions leading to incommensurately modulated ordered phases are described by order parameters with a minimum dimensionality 2, 4 or 6 resulting in single-q, double-q or triple-q structures. The NMR spectra of incommensurate systems with a two-component order parameter

$$Q_{\pm} = \varrho \exp(\pm i\phi) \tag{1}$$

– corresponding to a one-dimensional modulation wave with a phase $\phi = \vec{q}\vec{r} + \varphi_o$ and an amplitude ϱ – are by now well understood (1,2). Very little, on the other hand, is known (2,3,4) about the NMR lineshapes in incommensurate systems where the order parameter has four or more components such as biphenyl (4), barium sodium niobate (5), $BaMnF_4$(6), quartz (7) or many charge density wave compounds. In systems with a four component order parameter (4-6)

$$Q_{1\pm} = \varrho_1 \exp(\pm i\phi_1) \tag{2a}$$

and

$$Q_{2\pm} = \varrho_2 \exp(\pm i\phi_2) \tag{2b}$$

two rather different incommensurate states may exist. The first of these two possible state – $\varrho_1 = \varrho_2 \neq 0$ – corresponds to a "quilt" like structure with a simultaneous freezing of all four vectors $\pm\vec{q}_1$ and $\pm\vec{q}_2$ of the star of $\vec{k}$. It is incommensurately modulated along two different directions. Another possible state corresponds to a "stripe-like" domain structure with either $\varrho_1 = K \neq 0, \varrho_2 = 0$ or $\varrho_1 = 0, \varrho_2 = K \neq 0$, i.e. to a freezing of order parameter components associated with a single pair $\pm\vec{q}_1$ or $\pm\vec{q}_2$ of opposite wave vectors. Each domain is here modulated in a single direction but the direction of the modulation wave varies from one domain to the other. Several cases are known where the angle between the two moduloation directions $\vec{q}_1$ and $\vec{q}_2$ suddeenly changes and, e.g., a two-q structure becomes a single-q structure (4,5).

Here we wish to show how the NMR line-shape and relaxation rates depend on the ration $|\vec{q}_1/\vec{q}_2|$ and angle between the two $\vec{q}$ vectors for the case of a superposition of two incommensurate modulation waves.

Let us consider the case of a two dimensionally modulated incommensurate structure where the angle between the two modulation wave vectors $\vec{q}_1$ and $\vec{q}_2$ equals γ. The modulation wave is given by

$$u = u_{o1}\cos\varphi_1 + u_{o2}\cos\varphi_2 \tag{3}$$

where φ_1 and φ_2 can be expressed in the plane wave modulation approximation as

$$\varphi_1 = q_1 x \tag{4a}$$

and

$$\varphi_2 = (q_2 x)\cos\gamma + (q_2 y)\sin\gamma + \varphi_o. \tag{4b}$$

Let us further assume that the relation between the NMR frequency shift and the nuclear displacement is purely local and linear so that we have

$$\nu(\varphi_1, \varphi_2) = \nu_o + \nu_1\cos\varphi_1 + \nu_2\cos\varphi_2. \tag{5}$$

Here ν_1 and ν_2 are proportional to the amplitude of the incommensurate order parameters ϱ_1 and ϱ_2. φ_1 and φ_2 are independent and take on any value in the interval $[-\infty, +\infty]$ with equal probability.

Instead of sharp NMR lines as found in commensurate phases we should here have a frequency distribution $f(\nu)$ given by

$$f(\nu) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta\left[\nu - \nu(\varphi_1, \varphi_2)\right] d\varphi_1 d\varphi_2 = \int_{-\infty}^{+\infty} f_1(\nu') f_2(\nu - \nu') d\nu'. \quad (6)$$

Here $f_1(\nu)$ and $f_2(\nu)$ are the well-known frequency distributions for purely one dimensional modulations,

$$\nu = \nu_o + \nu_1 \cos\varphi_1 \quad (7a)$$

$$\nu = \nu_o + \nu_2 \cos\varphi_2 \quad (7b)$$

$$f_i(\nu') = \int_{-\infty}^{+\infty} \delta\left[\nu' - \nu(\varphi_i)\right] d\varphi_i = \frac{\text{const}}{d\nu'/d\varphi_i} = \frac{\text{const}}{\sqrt{\nu_i^2 - \nu'^2}}, \quad i = 1,2. \quad (8)$$

Expression (6) can be evaluated analytically in terms of elliptic functions. It is easy to see that for $\nu_1 = \nu_2$ the incommensurate frequency distribution $f(\nu)$ given by (6) exhibits an infinite logarithmic singularity at $\nu - \nu_o \to 0$:

$$f(\nu) \underset{\nu-\nu_o\to 0}{\approx} - \ell n[(\nu - \nu_o)/\nu_1]/\nu_1 \quad (9a)$$

and two step discontinuities at $\pm 2\nu_1$ (Fig.1a). This is in sharp contrast to the frequency distribution (8) for a one dimensional modulation (Fig.1b) where we have two edge singularities at $\nu - \nu_o = \pm\nu_1$.

It should be noted that the exact form of expression (6) is (ref.4):

$$f(\nu) \propto F\left[\arcsin\left(\frac{1-x}{1-x^2}\right), (1-x^2)^{1/2}\right] \quad (9b)$$

where $F(k, \varphi)$ is the elliptic integral of first kind with $k^2 = 1 - x^2$ and $x = \frac{\nu - \nu_o}{\nu_1}$.

It should be mentioned that for $\nu_1 \neq \nu_2$ we have – depending on the ration ν_1/ν_2 – a continuous transition from the $2q$ case with a central logarithmic singularity to the $1q$ case with two edge singularities.

It is interesting to note that $f(\nu)$ – as given by expression (8) – does *not* depend on the angle γ between the two modulation directions $\vec{q}_1$ and $\vec{q}_2$

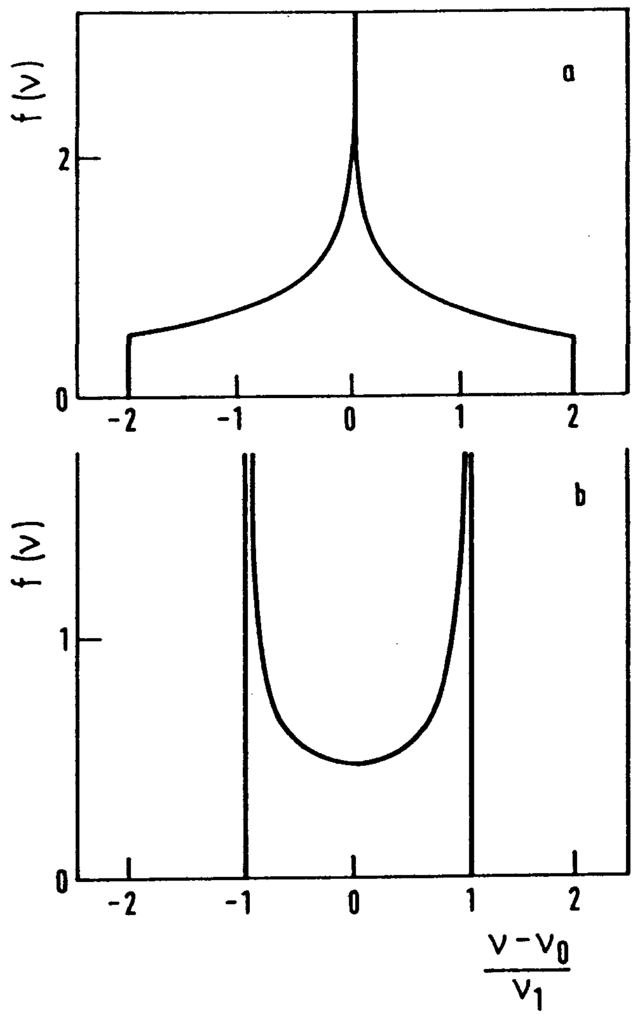

Fig. 1.

(a) NMR lineshape according to eq.(6) for a two-dimensional plane wave like modulation wave (5) with the two wave vectors $\pm\vec{q}_1$ and $\pm\vec{q}_2$ making an arbitrary angle $\gamma \neq 0$ ("quilt" phase).

(b) NMR lineshape for the "stripe phase" $\varrho_1 = 0, \varrho_2 = K$ and $\varrho_1 = K, \varrho = 0$ according to eq.(8).

as long as $\gamma \neq 0$. If $\gamma = 0$ so that $\vec{q}_1 || \vec{q}_2 || x$ and

$$\nu = \nu_o + \nu_1 \cos(q_1 x) + \nu_2 \cos(q_2 x + \phi_o) \qquad (10)$$

the frequency distribution is still given by expression (6) as long as $|\vec{q}_1|$ is incommensurate to $|\vec{q}_2|$

$$\left|\frac{\vec{q}_1}{|\vec{q}_2|}\right| \neq \frac{M}{N}, \quad M, N = 1, 2, 3 \ldots \qquad (11)$$

If however the ratio $|\vec{q}_1|/|\vec{q}_2$ is incommensurate, the lineshape depends on $|\vec{q}_1|/|\vec{q}_2|$.

For $|\vec{q}_2| = 2|\vec{q}_1|$, for example, where

$$\nu = \nu_o + \nu_1 \cos\varphi_1 + \nu_2 \cos(2\varphi_1) \qquad (12)$$

the lineshape is the same as for the case of a one-dimensional modulation wave where linear and quadratic terms are present in the expansion of ν in powers of the displacement.

It should be also noted that in the "stripe-like" incommensurate phase where we have domains $\varrho_1 = 0, \varrho_2 = K$ and $\varrho_1 = K, \varrho_2 = 0$ associated with the freezing of $\pm\vec{q}_1$ and $\pm\vec{q}_2$ respectively the NMR lineshape is given by expressions (8) (Fig.1b). This is due to the fact that the NMR lineshape does not depend on the direction of q as long as the associated displacements and frequency changes are the same. Recent deuteron NMR measurements of deuterated biphenyl (4) show that this is indeed the case.

Another unusual feature of systems with a four-dimensional order parameter is the spectrum of elementary excitations.

In the "quilt-like" phase ($\varrho_1 = \varrho_2$) one expects in the ideal case a double degenerate gapless phason, ω_{ph} (representing the modulatiuons $\delta\phi_1$ and $\delta\phi_2$ of the two phases ϕ_1 and ϕ_2) as well as two amplitudon modes, A_+ and A_-, representing the in phase, $\delta(\varrho_1 + \varrho_2)$, and out of phase, $\delta(\varrho_1 - \varrho_2)$ modulations of the amplitudes of the two modulation waves. In the "stripe-like" phase ($\varrho_1 \neq 0, \varrho_2 = 0$ or $\varrho_1 = 0, \varrho_2 \neq 0$), on the other hand, one expects both a normal amplitudon ω_A and gapless phason ω_{ph} corresponding to the frozen in one-dimensional modulation wave in a given domain ($\varrho_1 \neq 0$), as well as a doubly degenerate soft mode, ω_{d_m} corresponding to the modulation wave with $\varrho_2 = 0$. In both the "quilt-like" and the "stripe-like" phases one thus expects 3 order parameter modes but their nature is rather different.

In the "quilt-like" phase T_1^{-1} varies of the frequency distributions $f(\nu)$ in a way which is much more complicated than in the one-dimensionally modulated case. The edges of the spectrum at $\pm 2\nu_1$ will be relaxed by the amplitudons whereas the logarithmic singularity at $\nu - \nu_o \to 0$ will be relaxed by phasons and amplitudons. From the difference in T_1^{-1} at these two positions one can determine the spectral density of the phason and amplitudon modes, $J\varphi$ and $1/2(J_{A+} + J_{A-})$.

In deuterated biphenyl, where the incommensurate phase II is "stripe-like", one finds that:

$$T_1^{-1} = \left[\cos^2\varphi T_{1A}^{-1} + \sin^2\varphi T_{1\varphi}^{-1}\right] + T_{1d_m}^{-1} =$$
$$\left[(\frac{\nu - \nu_o}{\nu_1})^2\right] T_{1A}^{-1} + \left[1 - (\frac{\nu - \nu_o}{\nu_1})^2\right] T_{1\varphi}^{-1} + T_{1d_m}^{-1} \qquad (13)$$

Here $T_{1d_m}^{-1}$ is the relaxation contribution of the doubly degenerate soft mode whereas $T_{1\varphi}^{-1}$ and T_{1A}^{-1} refer to phason and amplitudon oscillations of the frozen out modulation wave. A fit of expressions (13) to the experimentally determined frequency variation of T_1 allows for a determination of $(T_{1A}^{-1} + T_{1d_m}^{-1})$ and $(T_{1\varphi}^{-1} - T_{1A}^{-1})$. Since far below T_I the amplitudon gap Δ_A is significantly larger than the gap of the doubly degenerate soft mode Δ_{d_m}, the effective relaxation rate depends here only on the phason and the doubly degenerate mode contributions. If the gap Δ_{d_m} of the doubly degenerate soft mode is known from independent measurements, one can use the T_1 data to determine the existence of a defect induced phason gap Δ_φ:

$$\frac{T_{1d_m}}{T_{1\varphi}} = \frac{\Delta_{d_m}}{\Delta_\varphi}. \qquad (14)$$

It should be also noted that in incommensurate systems not only T_1 but also T_2 and the adiabatic homogeneous linewidth $T_2'^{-1}$ vary over the incommensurate frequency distribution (8). The variation of the adiabatic width $T_2'^{-1}$, in particular, is completely analogous to the variation of T_1^{-1}:

$$\frac{1}{T_2'} \propto \left[x^2 j_A(0) + (1 - x^2) j_\varphi(0)\right] + j_{d_m}(0),$$
$$x = \frac{\nu - \nu_o}{\nu_1}, \qquad (15)$$

except for the fact that $T_2'^{-1}$ measures the spectral densities at zero frequency $j(0)$ whereas T_1^{-1} measures the spectral densities at the Larmor frequency $j(\omega_L)$.

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