Thermal Fluctuations and NMR Spectra of Incommensurate Systems

A. M. Fajdiga, T. Apih, J. Dolinšek, and R. Blinc
J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia

A. P. Levanyuk and S. A. Minyukov
Institute of Crystallography, Moscow, Russia, UIC

D. C. Ailion
Department of Physics, University of Utah, Salt Lake City, Utah 84112
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In the presence of thermal fluctuations the incommensurate NMR line shape is a convolution of a static inhomogeneous with a dynamic homogeneous line shape which can be determined separately by 2D NMR. The form of the dynamic line shape and its variation over the inhomogeneous NMR spectrum permit a separate determination of the relative sizes of the phason and amplitudon fluctuations, compared to the static part of the order parameter. ^{87}Rb 2D spectra of ultrapure Rb_2ZnCl_4 agree with the above theory and show the existence of a temperature range where the incommensurate splitting induced by the static part of the order parameter is averaged out by thermal fluctuations.

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Incommensurate insulators [1] are characterized by a modulation of the atomic positions with a periodicity that bears no simple rational relation to that of the underlying crystal lattice. For the simplest case of a one-dimensional modulation wave, the order parameter of the normal-to-incommensurate (N-I) transition is characterized by two components, the amplitude and the phase of the modulation wave. In contrast to the amplitude fluctuations (amplitudons), which become large only near the N-I transition, phase fluctuations (phasons) are significant over the entire incommensurate phase.

Whereas the static features of the incommensurate phase are reasonably well understood, this is not so for the dynamic aspects, especially in the vicinity of the temperature T_I of the N-I transition [1]. In particular, the effect of thermal fluctuations on the onset of incommensurate behavior and the possible floating of the modulation wave near T_I have been the subject of significant controversy. Furthermore, determination of the critical exponents, for example, requires a precise determination of T_I as well as a separation of the dynamic and static contributions to the modulation wave.

Because of its sensitivity to small displacements in the atomic positions, quadrupole-perturbed NMR, as well as nuclear quadrupole resonance (NQR), has been used extensively in the past [1,2] for studying the modulation wave in both dielectric [2] and charge-density-wave incommensurate systems [3,4]. Below T_I the NMR line becomes inhomogeneously broadened and acquires a specific shape that reflects the spatial distribution of the atomic positions in the modulation wave. Thermal fluctuations [5,6] significantly affect the shape of the NMR line. A number of experimental studies [5–11] have been devoted to the investigation of this effect. However, the experimental results do not agree with the theoretical calculations [5,6] predicting a motional narrowing of the NMR line but no other change in its Gaussian line shape. The disagreement may be due in part to an uncontrolled concentration of random impurities in the samples [11] and/or to certain approximations made in the calculations, such as the substitution of the time averaging of the fluctuating resonant frequency by averaging over a stationary Gaussian distribution of the phases of the modulation wave [5].

Here, we present a theory of the NMR line shape in incommensurate systems in the presence of thermal fluctuations of the order parameter. This theory is free of the above-mentioned approximations and is valid within the Landau theory [1]. It shows that thermal fluctuations not only reduce the linewidth but also change the shape of the spectrum in a characteristic way. Within a scaling factor, the line shape depends on just two parameters which are determined by the relative sizes of the phason and amplitudon fluctuations compared to the static part of the order parameter. We show that the line shape is given by a convolution of a static incommensurate frequency distribution and a dynamic line shape determined by phason and amplitudon order-parameter fluctuations. We have also shown how these two contributions can be simultaneously independently determined by two-dimensional (2D) nuclear magnetic resonance. The theoretical results agree well with a 2D ^{87}Rb NMR study of Rb_2ZnCl_4, obtained with high temperature resolution. The separate simultaneous determination of the static (inhomogeneous) and dynamic (homogeneous) line shapes allows a precise determination of T_I and clearly shows the presence of a region where thermal fluctuations of the modulation wave average out the quadrupolar splitting due to the static part of the order parameter.

Let us consider the case of a one-dimensionally modulated incommensurate system with a two-component order parameter [1,2]. Just below T_I where the plane wave approximation [1] is valid, the incommensurate distortion wave $\eta(x)$ can be expressed as

$$\eta(x)=\eta_1\cos(k_0x)+\eta_2\sin(k_0x)\,, \tag{1}$$

where η_1 and η_2 are the two components of the order parameter [1,12] describing the *N-I* transition and k_0 is the wave vector of the incommensurate modulation. Thermal fluctuations of the order parameter result in

$$\eta_1(x,t)=\eta_{1E}+\eta_1'(x,t)\,, \tag{2a}$$

$$\eta_2(x,t)=\eta_{2E}+\eta_2'(x,t)\,. \tag{2b}$$

For the equilibrium values η_{1E} and η_{2E} we can take [1] $\eta_{1E}^2\propto(T_I-T)$ and $\eta_{2E}=0$. Let us now assume that the quadrupole perturbed NMR resonance frequency Ω of a nucleus at a site x is linearly related [1,2] to the nuclear displacement $\eta(x,t)$ at this site:

$$\Omega(x,t)=\Omega_0+a\eta(x,t)\,. \tag{3}$$

Here $\eta(x,t)$ is given by expressions (1), (2a), and (2b). The adiabatic NMR line shape $I(\omega)$ is now obtained [13] as

$$I(\omega)=\int_0^\infty G(t)e^{i\omega t}dt\,, \tag{4a}$$

where

$$G(t)=e^{-i\Omega_0 t}\left\langle\left\langle\exp\left[-i\int_0^t[\Omega(x,t')-\Omega_0]dt'\right]\right\rangle\right\rangle_x\,. \tag{4b}$$

The inner brackets $\langle\,\rangle$ represent a thermodynamic ensemble average whereas $\langle\,\rangle_x$ stands for an average over the inhomogeneous static distribution of resonance frequencies. Inserting expression (3) into (4b) we find the autocorrelation function $G(t)$ in the form

$$G(t)=e^{-i\Omega_0 t}\langle\langle G_1(t)G_2(t)\rangle\rangle_x\,. \tag{5}$$

Here

$$G_1(t)=\exp[-ia\eta_{1E}t\cos(k_0x)] \tag{6}$$

represents the well known [1,2] static inhomogeneous frequency distribution limited by two edge singularities, whereas

$$G_2(t)=\exp\left[-ia\int_0^t[\eta_1'(x,t')\cos(k_0x)+\eta_2'(x,t')\sin(k_0x)dt'\right] \tag{7}$$

describes the effects of amplitudon $[\eta_1'(x,t)]$ and phason $[\eta_2'(x,t)]$ fluctuations on the NMR line shape. Since the product of two functions in the time domain is equivalent to the convolution of their Fourier transforms in the frequency domain, the Fourier transform of G_2 represents the dynamic line shape which convolutes the static [1,2] one. After a straightforward [13] but somewhat lengthy calculation one finds the adiabatic line shape in the incommensurate phase as

$$I(\omega)=\int_{-1}^{+1}\frac{d\chi}{(1-\chi^2)^{1/2}}\int_0^\infty dt\,e^{i(\omega-\Omega_0-\Omega_1\chi)t}e^{-[\omega_{\mathrm{loc}1}t\chi^2+(\omega_{\mathrm{loc}2}t)^{3/2}(1-\chi^2)]}\,, \tag{8}$$

where

$$\chi=\cos(k_0x),\quad \Omega_1=a\eta_{1E}\,,$$

$$\omega_{\mathrm{loc}1}=\frac{a^2k_BT\gamma r_c}{4\pi\delta^2}\propto\frac{T}{(T_I-T)^{1/2}}\,,$$

and

$$\omega_{\mathrm{loc}2}=\left[\frac{a^2k_BT\gamma^{1/2}}{24\pi^{3/2}\delta^{3/2}}\right]^{2/3}\propto T^{2/3}\,.$$

Here δ is the coefficient of the elastic term in the Landau free-energy expansion [1], γ is the coefficient in front of the dissipation function $[(\gamma/2)(\dot\eta_1^2+\dot\eta_2^2)]$, and r_c is the correlation radius [1] for the amplitude of the modulation wave. Expression (8) cannot be evaluated analytically because of the $t^{3/2}$ term, representing the phason contribution. Up to a scaling factor $I(\omega)$ depends on just two parameters,

$$\xi_1=\frac{\omega_{\mathrm{loc}1}}{\Omega_1}\propto\frac{T}{T_I-T}$$

and

$$\xi_2=\frac{\omega_{\mathrm{loc}2}}{\Omega_1}\propto\frac{T^{2/3}}{(T_I-T)^{1/2}}\,,$$

which measure the relative size of amplitudon and phason order-parameter fluctuations compared to the static order parameter. Far below T_I, ξ_1 and ξ_2 tend to zero, $\langle G_2(t)\rangle\rightarrow 1$, and $I(\omega)$ is reduced to the static incommensurate frequency distribution [1]

$$I(\omega)=\frac{1}{\{1-[(\omega-\Omega_0)/\Omega_1]^2\}^{1/2}}\,, \tag{9}$$

which exhibits two edge singularities at $\pm\Omega_1$.

It is important to note that 2D NMR allows a simultaneous separate determination [14] of the inhomogeneous line shape, represented by $\langle G_1G_2\rangle$, and the dynamic line shape, represented by $\langle G_2\rangle$. This is achieved by the application of a 180° refocusing pulse [14] in the middle of the evolution period.

The 2D NMR line shape is obtained as

$$I(\omega_1,\omega_2)=\int_{-1}^{+1}\frac{d\chi}{(1-\chi^2)^{1/2}}\int_0^\infty dt_1\int_0^\infty dt_2 e^{i(\omega_2-\Omega_0-\Omega_1\chi)t_2}e^{-[\omega_{\mathrm{loc}1}t_2\chi^2+(\omega_{\mathrm{loc}2}t_2)^{3/2}(1-\chi^2)]}e^{i\omega_1t_1}e^{-[\omega_{\mathrm{loc}1}t_1\chi^2+(\omega_{\mathrm{loc}2}t_1)^{3/2}(1-\chi^2)]}\,, \tag{10}$$

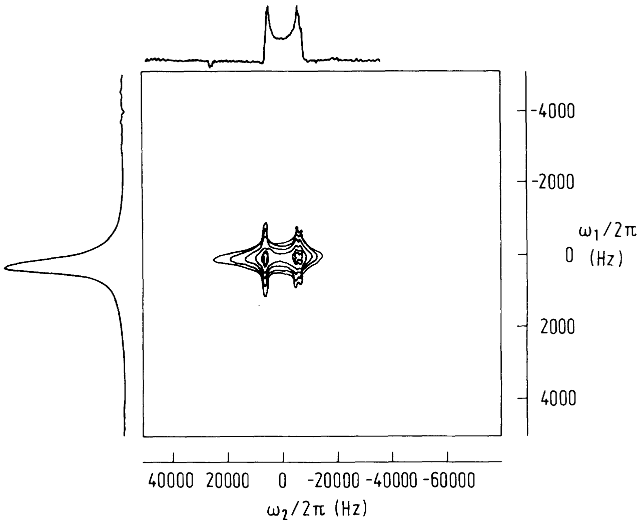

FIG. 1. 2D "separation of interactions" NMR spectrum [14] of the ^{87}Rb $\frac{1}{2} \to -\frac{1}{2}$ transition in Rb_2ZnCl_4 at an orientation $\mathbf{a} \perp \mathbf{H}_0$, $\measuredangle \mathbf{c},\mathbf{H}_0 = 122°$, and $T = 291.2$ K. Projections on both frequency axes are also shown. The ^{87}Rb Larmor frequency is $\nu_L(^{87}\mathrm{Rb}) = 88.34$ MHz.

where t_1 is the evolution and t_2 the detection time [14] in the 2D experiment (Fig. 1).

A high-temperature-resolution 2D NMR ^{87}Rb $\frac{1}{2} \to -\frac{1}{2}$ transition study [14] of ultrapure Rb_2ZnCl_4 has been made in the vicinity of the N-I transition in steps of 0.1 K. In the ω_2 domain we find the static inhomogeneous line shape convoluted with the dynamic one (Fig. 1). In the ω_1 domain the static quadrupole interaction is eliminated [14] and the homogeneous dynamic line shape is determined by the time-fluctuating part of the quadrupole interaction (Fig. 1). The dynamic line shape varies over the inhomogeneous static incommensurate frequency distribution through its dependence on $\chi = \cos(k_0 x) = (\omega_2 - \Omega)/\Omega_1$. In the center of the inhomogeneous line where $\chi = 0$, the dynamic line shape is determined by phason fluctuations (i.e., by the $t^{3/2}$ term). At the edge singularities, where $\chi = \pm 1$, the dynamic line shape is determined by amplitudon fluctuations (i.e., the t term), yielding a Lorentzian form.

In Fig. 2 we show the temperature dependence of the positions of the edge singularities of the inhomogeneous line shape obtained in the ω_2 domain on the Rb line centered around $\omega_2 = 0$ (Fig. 1). The full width at half height of the dynamic line shape obtained in the ω_1 domain in the center of the inhomogeneous line shape (i.e., at $\omega_2 = \Omega$) is also shown. On the same plot we also show the temperature dependences of the soft mode as well as phason ($T_{1\varphi}$) and amplitudon (T_{1A}) induced spin-lattice relaxation rates [1,2]. It is clearly seen that the width of the dynamic line shape exhibits a maximum at $T_I = 304.4$ K. At the same temperature the T_1 splits [1,2] into two branches, the temperature-independent phason contribution and the critically temperature-

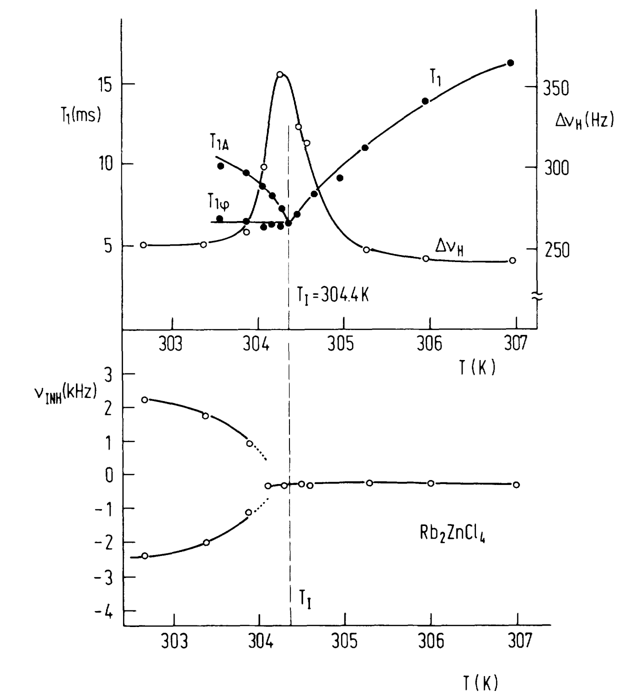

FIG. 2. The lower part of the figure shows the temperature dependence of the frequencies of the incommensurate edge singularities, ν_{INH}, of the inhomogeneous line shape. The upper part shows the temperature dependence of the full width at half height of the homogeneous dynamic line shape, $\Delta\nu_H$, in the center of the inhomogeneous spectrum. The temperature dependence of the soft mode (T_1), phason ($T_{1\varphi}$), and amplitudon (T_{1A}) induced spin-lattice relaxation times is shown for comparison.

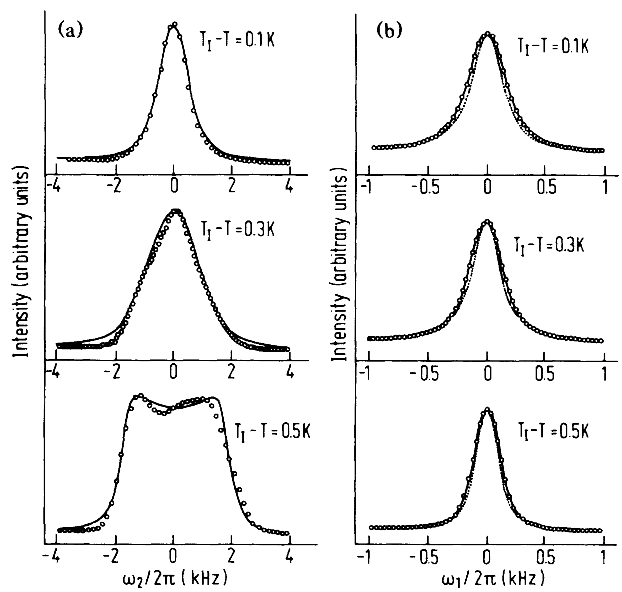

FIG. 3. (a) Inhomogeneous and (b) homogeneous dynamic line shapes close to T_I. The solid lines in (b) show the fit to expression (10), whereas the dotted line is the fit to a Lorentzian.

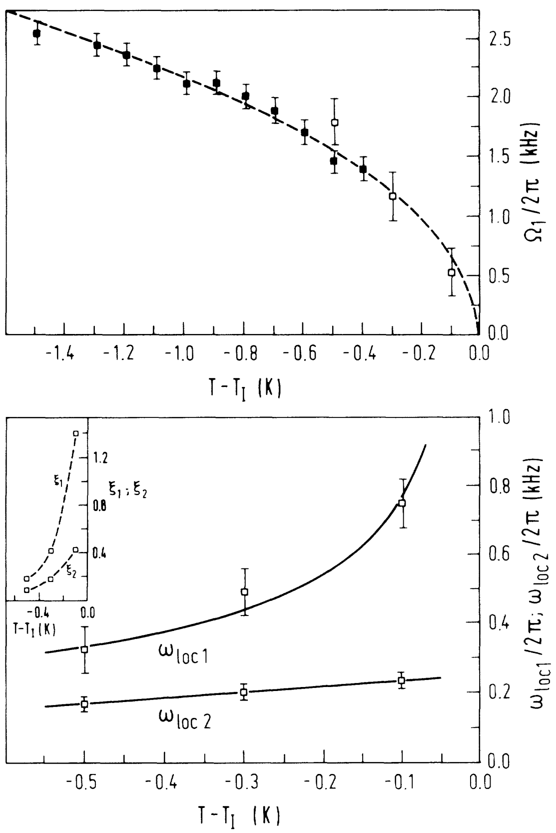

FIG. 4. Temperature dependence of the parameters $\omega_{\mathrm{loc}1}/2\pi$, $\omega_{\mathrm{loc}2}/2\pi$, and $\Omega_1/2\pi$ obtained from a least-squares fit by comparing experimental and theoretical inhomogeneous and homogeneous line shapes (open squares). The additional Ω_1 points (solid squares) are obtained from the edge singularity data in the temperature range between $T_I-T=0.4$–1.5 K. The dashed line represents a least-squares fit $\Omega_1 \propto (T_I-T)^z$ with $z=0.5$. Inset: The normalized quantities $\xi_1=\omega_{\mathrm{loc}1}/\Omega_1$ and $\xi_2=\omega_{\mathrm{loc}2}/\Omega_1$ which measure the relative sizes of the fluctuating and static parts of the incommensurate order parameter.

dependent amplitudon contribution. The temperature T_I is clearly the *N-I* phase transition temperature where the paraelectric soft mode condenses, resulting in a maximum width of the dynamic line shape. In contrast the inhomogeneous line shape shows no splitting at this temperature. The incommensurate splitting starts to become observable only at $T_I-T \geq 0.4$ K, i.e., outside the region where motional narrowing due to thermal fluctuations of the modulation wave is dominant.

The inhomogeneous and the dynamical line shapes are shown in Fig. 3 at $T_I-T=0.1$, 0.3, and 0.5 K. At $T_I-T=0.1$ and 0.3 K the inhomogeneous line shape is still single peaked whereas the two edge singularities become clearly discernible at $T_I-T=0.5$ K [Fig. 3(a)]. The experimental and theoretical dynamic line shapes are compared in Fig. 3(b). The deviations of the dynamic line shapes from a Lorentzian form show the importance of the phason fluctuations represented by the $t^{3/2}$ term. The comparison between the experimental and theoretical line shapes allows for a determination of the parameters ξ_1 and ξ_2 from $\omega_{\mathrm{loc}1}=C[T/(T_I-T)^{1/2}]$, $\omega_{\mathrm{loc}2}=DT^{3/2}$, and Ω_1, which are shown in Fig. 4 as functions of temperature. We find that $C=(5\pm0.3)\times10^{-3}$ $\mathrm{s}^{-1}\mathrm{K}^{-1/2}$ whereas $D=31\pm3$ $\mathrm{s}^{-1}\mathrm{K}^{-2/3}$. Ω_1 varies with temperature as $\Omega_1 \propto (T_I-T)^z$, where $z=0.5$ as predicted by the Landau theory. It should be noted that Ω_1, which is proportional to the amplitude of the frozen-in modulation wave, becomes comparable to $\omega_{\mathrm{loc}1}$ and $\omega_{\mathrm{loc}2}$, which measure the fluctuating parts of the order parameter about 0.1 K below T_I.

We can conclude that the adiabatic incommensurate NMR line shape is indeed given by the Fourier transform of $\langle G\rangle = \langle G_1 G_2\rangle$ and not just G_1 as tacitly assumed so far in all NMR studies of incommensurate phase transitions. The fluctuation correction, G_2, which is somewhat similar to the Debye-Waller factor in x-ray scattering, determines the form of the NMR spectrum close to T_I.

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