Deuteron NMR and soliton density in incommensurate thiourea

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The deuteron nuclear magnetic resonance spectra of thiourea, $SC(ND_2)_2$, show a gradual change of the incommensurate modulation wave from the plane wave to the soliton type. This demonstrates that even in type II incommensurate systems where there is no Lifshitz invariant and where it has been generally assumed until recently that the modulation wave is always of the plane wave type, a soliton regime can indeed take place. The behavior of type II incommensurate systems is in this sense thus not fundamentally different from that of type I systems with a nonzero Lifshitz term.

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I. INTRODUCTION

Thiourea, $SC(NH_2)_2$ and its deuterated form, $SC(ND_2)_2$, represent a special case where a type II incommensurate (IC) phase has been suggested to exhibit a multi-soliton regime.[1,2]

Whereas soliton regimes have been reported[3,4] in the past in type I incommensurate systems where the order parameter is at least two-dimensional and a Lifshitz invariant[5,6] drives the system to an modulated incommensurate phase,[7] this is not the case with type II incommensurate systems such as thiourea. Here the soft mode instability occurs close to the Brillouin zone center. Therefore, the order parameter is one dimensional and there is no Lifshitz invariant.[5–7] In the free energy density expansion of such systems[8] there are no terms that lead to a sine-Gordon equation and produce solitons. It has been generally assumed until recently[7,9] that the incommensurate modulation of type II systems is always of the plane wave nature. This should be true down to the lock-in transition to the commensurate phase without any intermediate multi-soliton lattice regime.

Zuñiga *et al.*[1] observed by x-ray scattering a soliton-like form for the atomic modulation function of thiourea. The same is true[2] for the structural study of Tanisaki and Mashiyama.[2] The amplitude of the third order harmonic was found to be as high as 25% of that of the first harmonic. The modulation functions showed a soliton step-like profile with two steps as expected for a lock-in transition at $\vec{q}=0$.[10] The soliton density was estimated to be around 0.5 just before the lock-in transition takes place.[11] The molecular translational modulation function along the x axis, on the other hand, remained sinusoidal, i.e., plane wave-like over the whole I phase. Soliton-like and sinusoidal IC structural modulation thus coexists in thiourea.[11]

A possible theoretical explanation of this situation was given by Aramburu, Madariaga, and Perez-Mato.[11] The explanation is based on a numerical analysis of the free energy density for type II IC systems proposed by Levanyuk and Sannikov.[8] They introduced the coupling of the one-dimensional order parameter η for type II IC systems with a secondary parameter ξ which transforms as $d\eta/dy$ where y is the spatial coordinate along the modulation direction. The IC phase is here given by two parameters $\eta(y)$ and $\xi(y)$ as in type I systems, whereas the lock-in phase is described by $\eta=0$ and $\xi=0$.

The distorsions η and ξ are strongly coupled in the IC phase. They can be parametrized[11] by a common phase $\theta(y)$

$$\eta(y) = \rho \cos[\theta(y)], \tag{1}$$

$$\xi(y) = \rho' \sin[\theta(y)], \tag{2}$$

which acquires a sine-Gordon solitonic form in the vicinity of the lock-in transition if higher order terms can be neglected. In contrast to type I IC systems, the sine-Gordon equation is here not the exact differential equation for the phase of the modulation wave but seems to represent a rather good approximation.[11]

It is the purpose of this paper to check on the soliton regime and the general nature of the modulation wave in thiourea by quadrupole perturbed deuteron nuclear magnetic resonance (NMR), i.e., by a technique which is independent and rather different from the scattering techniques[1,2] used so far in thiourea. We also wished to determine the temperature dependence of the soliton density. The NMR technique has been used extensively to determine the soliton density in type I IC systems.[3,4]

Still another reason to perform a deuteron NMR study of thiourea is the fact that the rigid body modulation model of the IC phase of thiourea[1,2] is consistent only if the H atoms were not included. The possibility of rotations of the NH_2 groups with respect to the rest of the thiourea molecule can thus not be excluded. The deuteron NMR study of thiourea, on the other hand, measures selectively only the modulation function of the NH_2 groups.

II. EXPERIMENT

The experiment was performed on the single crystal grown in the Institute of Physics ASCR (Prague) by the slow evaporation method from deuterated methanol solution under

same conditions as the crystals used in recent inelastic neutron[12] and light scattering[13] studies.

The Fourier transform deuteron NMR spectra of a $SC(ND_2)$ single crystal have been measured at a Larmor frequency $\omega/2\pi=30.71$ MHz in a magnetic field $B_0=4.7$ T as a function of temperature and crystal orientation. The solid echo pulse sequence was used. The width of the 90° pulse was 10 μs. Both the free induction decay and the spin echo Fourier transform spectra were studied.

Thiourea undergoes a phase transition from the paraelectric room temperature phase with space group *Pnma* and four molecular units per unit cell, $z=4$, to an IC phase at 200 K. In the high temperature phase the spectrum consists of four lines which are broadened at the transition to the incommensurate phase. An orientation, at which those transitions do not overlap, was chosen. The modulation direction is along the b axis. Between 169 and 171 K the modulation locks into a commensurate value $\vec{q}=\vec{b}^*/9$. Below 169 K the crystal transforms into a nonmodulated ferroelectric phase ($\vec{q}=0$) with the space group $P2_1ma$. The corresponding phase transition temperatures for the deuterated form, $SC(ND_2)_2$ are[14] 218, 193, and 191 K.

The deuteron ($I=1$) NMR spectrum in the presence of a nonzero quadrupole coupling always consists of two transitions, $1\leftrightarrow 0$, and $0\leftrightarrow -1$. For the study of the incommensurate phase we have concentrated on only one of these two transitions.

III. THEORY OF THE NMR LINE SHAPE

The displacement of the molecule j in the unit cell l due to the frozen in incommensurate soft mode can be expressed as[14]

$$u_{l,j}=\rho\sum_{\lambda=1,3,5}a_\lambda s_\lambda(j)\cos(\vec{q}_\delta\cdot\vec{r}_{lj}+\varphi)+\rho\sum_{\lambda=2,4,6}a_\lambda s_\lambda(j)\sin(\vec{q}_\delta\cdot\vec{r}_{lj}+\varphi). \tag{3}$$

Here ρ and φ are the amplitude and phase of the frozen out soft mode and $s_\lambda(j)$ are symmetry adapted eigenvectors.[9] The sine-wave component is small compared to the cosine wave. Here rotation is the dominant term, whereas translational terms are smaller.[11]

Since the N–D bond in the $SC(ND_2)_2$ molecule is of covalent nature, the resonance frequency of a given nucleus ν_i will depend only on the displacement of the resonating nucleus and the displacements of the other atoms in the rigid thiourea molecule moving in phase with it as well as on the possible rotation of the N–D bond with respect to the rest of the molecule.

In view of that we are in the "local" case where

$$\nu_i=\nu[u_i(y)] \tag{4}$$

and y is the spatial coordinate in the direction of the modulation.

This relation can be expanded in powers of the displacements $u_i(y)$

$$\nu_i=\nu_0+c_1u_i(y)+\frac{1}{2}c_2u_i^2(y)+\ldots_i \tag{5}$$

yielding

$$\nu_i=\nu_o+\nu_1\cos[\phi(y)+\phi_0]+\frac{1}{2}\nu_2\cos^2[\phi(y)+\phi_0]+\ldots. \tag{6}$$

Here ϕ_0 is an initial phase and $\phi(y)=\vec{q}_0\vec{r}_{lj}+\psi(l)$ where $\vec{r}_{lj}=\vec{y}_{0j}+l\cdot\vec{b}$, $l=0,1,2,3,\ldots$ with $\vec{y}_{0j}$ denoting the position of the jth nucleus in the lth unit cell. In the continuum approximation $\psi(y)$ is a solution of the sine-Gordon equation and $\cos[\phi(y)]$ takes on nearly continuously all values between +1 an −1. The temperature variation of ν_1 is determined by the amplitude of the modulation wave and thus by the critical exponent β

$$\nu_1\propto\rho\propto(T_I-T)^\beta. \tag{7}$$

Here T_I is the paraelectric to IC phase transition temperature. The intensity of the resonance line in the frequency interval between ν and $\nu+d\nu$ is proportional to the number of nuclei resonating in this interval. Knowing the function $\nu=\nu[u(y)]$, i.e., knowing the dependence of ν on the coordinate y in the direction of the modulation, one can calculate the frequency distribution function $f(\nu)$ and compare the experimental data with theoretical predictions. Alternatively from the measured $f(\nu)$ we can get some information on $\nu=\nu[u(y)]$ and the nature of the modulation wave.

For the case of a one-dimensional incommensurate (I) modulation we find in the constant amplitude approximation in the linear case ($\nu_1\neq 0$, $\nu_2=0$)

$$f(\nu)=\frac{\text{const}}{d\nu/dy}=\frac{\text{const}}{(d\nu/d\phi)(d\phi/dy)}. \tag{8}$$

Singularities will appear when $d\nu/d\phi\rightarrow 0$ or when $d\phi/dy\rightarrow 0$.

If the modulation is of the "plane wave" type, $d\phi/dy=$const and we find

$$f(\nu)=\frac{\text{const}}{\sqrt{\nu_1^2-(\nu-\nu_0)^2}}. \tag{9}$$

The spectrum is here limited by two edge singularities at $\nu-\nu_0=\pm\nu_1$. The splitting between these edge singularities increases with the critical exponent β

$$\Delta\nu=2\nu_1\propto\rho\propto(T_1-T)^\beta. \tag{10}$$

The actual line shape $F(\nu)$ will be given by a convolution of $f(\nu)$ with the spectral function $L(\nu-\nu')$ determining the linewidth in the paraelectric phase

$$F(\nu)=\int f(\nu')L(\nu-\nu')d\nu'. \tag{11}$$

In the "multi-solution" lattice case, ϕ is a nonlinear function of y. The function ϕ will be nearly constant in the commensurate domains where $(d\phi/dy)\rightarrow 0$ resulting in new "commensurate" lines and the reduction of the intensity of the

incommensurate background and edge singularities.

From the sine-Gordon equation one finds in the case type I IC systems

$$\left(\frac{d\phi}{dy}\right)^2 = \text{const.}\sqrt{\Delta^2 + \cos^2[N(\psi(y) - \phi_o)]/2}. \quad (12)$$

For $\Delta \to 0$ we find up to N new "soliton" lines when $\cos^2[N(\psi - \phi_0)/2 = 0]$, i.e., when

$$\psi = (2m+1)\pi/N + \phi_0, \quad m = 0,1,2,\ldots N-1. \quad (13)$$

The edge singularities, on the other hand, appear when ψ is an integer multiple of π.

Here $\psi(y) = \phi(y) + \phi_0$.

The soliton density n_s, i.e., the fraction of the crystal volume where ϕ is a nonlinear function of y, is now obtained[3,4] as

$$n_s = \frac{\pi/2}{K(k)}, \quad (14)$$

where

$$k^2 = \frac{1}{1+\Delta^2} \quad (15)$$

and $K(k)$ is the complete elliptic integral of the first kind.

A fit of the experimental $f(\nu)$ to the theoretical line shape allows here for a determination of the volume fraction of the crystal in the incommensurate domain walls, i.e., the soliton density n_s.

For type I IC systems, the minimization of the Euler–Lagrange equations of the free energy density yields[11] for $\rho = \rho'$ an equation for the phase θ

$$\left(\frac{d\theta}{dy}\right)^2 = a_0 + a_1\cos(2\theta) + a_2\cos(4\theta) + \ldots \quad (16)$$

which reduces for thiourea in a rather good approximation to the sine-Gordon equation

$$\left(\frac{d\theta}{dy}\right)^2 = \tilde{A}^2[1 - k^2\cos^2\theta]. \quad (17)$$

The soliton density n_s is here again given by expression (14). The solution for the phase θ becomes step-like as $k \to 1$.

In a higher order commensurate C phase, where the modulation vector δ locks-in into a rational value, $\phi(y)$ becomes a constant which renormalizes ϕ_0 and we get in the linear case

$$\nu = \nu_0 + \nu_1\cos\left(2\pi\frac{M}{N} + \phi_0\right), \quad M = 0,1,2\ldots N-1. \quad (18)$$

Here M, N are integers. We assumed that the commensurate unit cell is N-times larger than the high temperature unit cell. In the case of thiourea we thus have $N=9$.

The frequency distribution $f_C(\nu)$ in the C phase with N nonequivalent sites per unit cell is a sum of delta functions

$$f_C(\nu) = \frac{1}{N}\sum_{M=0}^{N-1}\delta\left[\nu - \nu_o - \nu_1\left(\cos 2\pi\frac{M}{N} + \overline{\phi_0}\right)\right] \quad (19)$$

yielding for each line in the high temperature phase N commensurate lines in the C phase instead of the quasi-continuous incommensurate frequency distribution $f(\nu)$.

In fact, we still have to convolute $f_C(\nu)$ with the shape $L(\nu - \nu_C)$ of each single line. Thus we get

$$F(\nu) = \int_{-\infty}^{+\infty} L(\nu - \nu_C) f(\nu_C)\mathrm{d}\nu_C. \quad (20)$$

If $L(\nu - \nu_C)$ is Gaussian, the above integral becomes

$$F(\nu - \nu_0) = \frac{1}{N}\sum_{M=0}^{N-1}\frac{1}{\sqrt{2\pi\sigma}}\exp\left\{-\left[\nu - \nu_0 - \nu_1\left(\cos 2\pi\frac{M}{N} + \bar{\phi}_0\right)\right]\Big/ 2\sigma^2\right\}, \quad (21)$$

where $\sqrt{2}\sigma$ is the width of the line in the high temperature phase. The C lines will become smeared and indistinguishable from the incommensurate line shape if

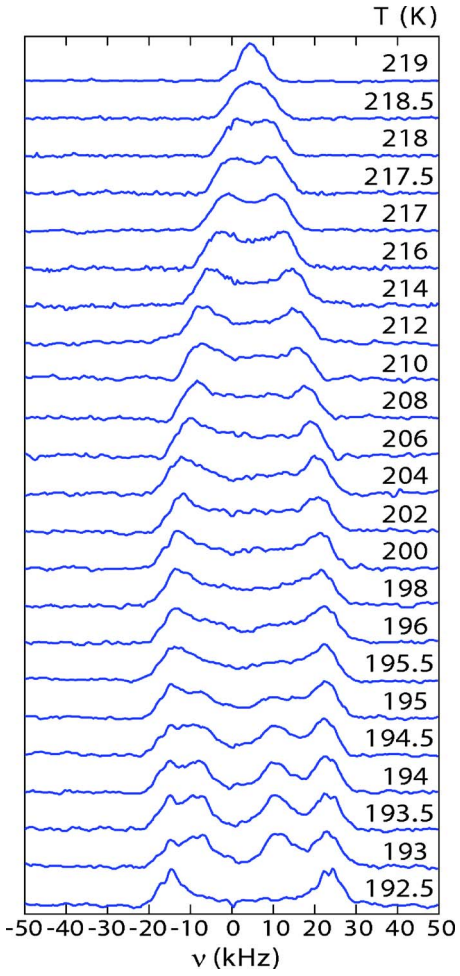

FIG. 1. (Color online) Deuteron NMR spectra of a $SC(ND_2)_2$ single crystal at an orientation where the linear term is dominant.

$$\sqrt{2}\sigma > 2\nu_1/(N-1). \quad (22)$$

This is the limit for the NMR discrimination between the I and higher order C phases. The difference in line shape between the IC and the C phase with $N=9$ is thus expected to be rather small and hardly discernible experimentally.

IV. RESULTS AND DISCUSSION

Since we are mainly interested in the problem of the existence or nonexistence of a soliton regime in thiourea, we selected an orientation where the spectra are as simple as possible and where the linear term in the expansion of the NMR frequency in powers of the IC displacement is dominant.

The temperature dependence of the N–D deuteron NMR spectra are shown in Fig 1. The single narrow NMR line of the paraelectric phase changes into an inhomogeneous frequency distribution $f(\nu)$ below T_I in the IC phase. The frequency distribution can be here described by expressions [9,11]. The typical IC line shape with two smeared out edge singularities appears already at 218–217.5 K. The separation between the edge singularities $\Delta\nu$ increases with decreasing temperature according to expression (10), (Fig. 2). From the plot of $\log \Delta\nu$ vs $T_I - T$ (inset to Fig. 2) we obtain the critical exponent for the amplitude of the IC modulation wave as $\beta = 0.35 \pm 0.02$. The soliton structure in the spectrum starts to show up below 200 K and is already well pronounced at 195–194.5 K. The main effect is the appearance of two asymmetrically located soliton peaks in addition to two incommensurate edge singularities. The soliton peaks are due to that part of the crystal where $d\theta/dy \to 0$ due to the nonlinear dependence of the phase θ on the spatial coordinate in the direction of the modulation y.

The fit with the linear term $\nu = \nu_o + \nu_1 \cos[\phi(y) + \phi_0]$ with $\nu_1 = \nu_{1,0}\left(\frac{T_I - T}{T_I}\right)^{\beta}$ in the expansion of the frequency in powers of the displacement is good in the high temperature part of the incommensurate phase where the modulation is of the plane wave type. At lower temperatures, where the modulation is multi-soliton like, an additional small but nonzero quadratic term—of the order of 10% of the linear term—had to be added to the expansion to take into account the slight asymmetry of the line shape. When this term is taken into account, the fit becomes nearly perfect.

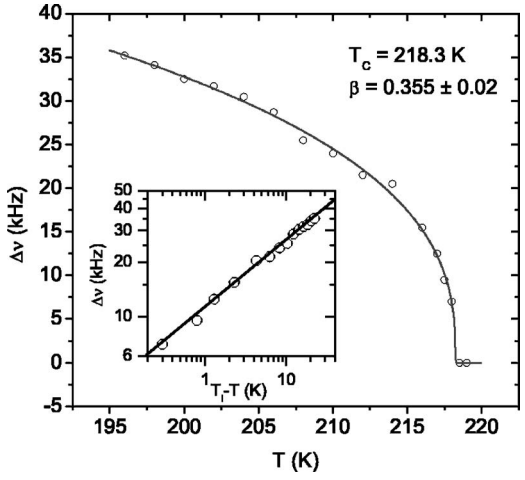

FIG. 2. Temperature dependence of the splitting between the two edge singularities. The inset shows the $\log(\Delta\nu)$ vs $(T_I - T)$ plot allowing for the determination of the critical exponent $\beta = 0.35 \pm 0.02$.

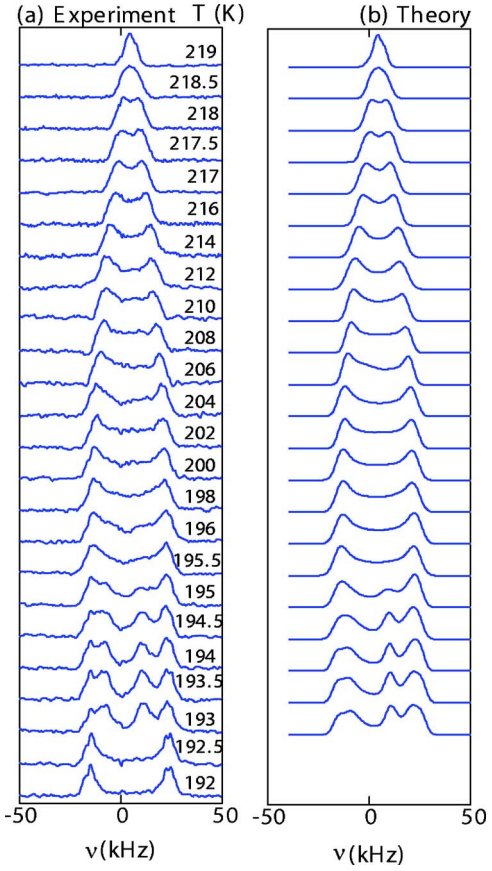

FIG. 3. (Color online) Comparison between the experimental (a) and theoretical (b) deuteron NMR line shapes showing the transition into the soliton regime at lower temperatures. Here the linear term is $\nu_1 = \nu_{1,0}\left(\frac{T_I - T}{T}\right)^{\beta}$ with $\nu_{1,0} = 44.85$ kHz, $\beta = 0.35$, and $T_I = 218.3$ K. The value of quadratic term is about 10% of the value of the linear term in the low temperature part of the incommensurate phase.

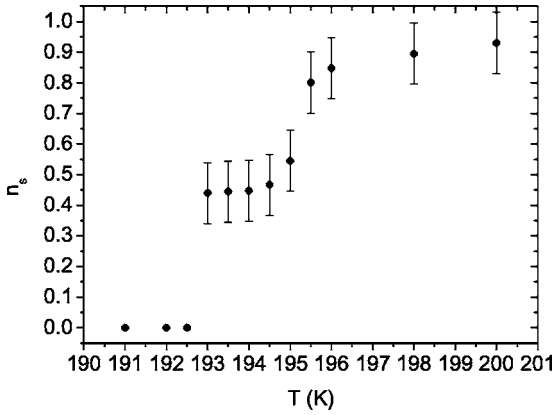

FIG. 4. Temperature dependence of the soliton density in deuterated thiourea.

The experimental IC line shapes and the theoretical fits are compared in Fig. 3. The gradual change from the plane wave-type modulation to the soliton limit is evident.

The temperature dependence of the experimentally determined soliton density n_S is presented in Fig. 4. Down to 200 K we are in the pure plane wave limit where $n_S=1$. Below 200 K the spectra become characteristic of the "broad" soliton limit. At still lower temperature we come to the "narrow" soliton regime and n_S reaches 0.58 at 194.5 K. Below that the apparent value of n_s becomes approximately 0.55 in the commensurate phase with $\vec{q}=\vec{b}^*/9$. Here the spectrum essentially consists of nine overlapping commensurate lines.

The frequency distribution and all IC features of the NMR spectra disappear below 192.5 K where we obviously enter the ferroelectric phase. The spectrum here consists of two sharp lines instead of a single one due to a rotation of the ND_2 group.

The above results thus show that type II IC systems without a Lifshitz invariant can exhibit an incommensurate soliton-type modulation regime similar to the one found in type I IC systems like $RbZnCl_4$ and others.[3] The present data support the theoretical results of Aramburu, Madariaga, and Perez-Mato[11] for type I IC systems. In addition, they show that the critical exponent for the amplitude of the modulation wave in thiourea is nonclassical and equals $\beta=0.35\pm0.02$.

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