Soliton Density in Structurally Incommensurate Systems

R. Blinc, V. Rutar, B. Topič, F. Milia,[a] and I. P. Aleksandrova[b]
J. Stefan Institute, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia

and

A. S. Chaves and R. Gazzinelli
Departamento de Fisica, Universidade Federal de Minas Gerais, C.P. 702, Belo Horizonte, Brazil

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The temperature variation of the phase soliton density has been determined in Rb_2ZnCl_4 and a nonclassical critical exponent $\frac{1}{2}$ has been found. Electron-paramagnetic-resonance and nuclear-magnetic-resonance data demonstrate that in K_2SeO_4, Rb_2ZnCl_4, and Rb_2ZnBr_4 the soliton width is large as compared to the intersoliton spacing over most of the incommensurate phase so that the continuum description is adequate.

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Structurally incommensurate (I) systems are characterized by the appearance of a mass-density wave (i.e., a modulated lattice distortion) with a periodicity which is an irrational fraction of the periodicity of the underlying lattice. In the "plane-wave" modulation limit the incommensurate distortion is characterized by a single Fourier component of the displacement. A refined Landau theory[1-3] has shown that this solution is not stable well below the paraelectric-incommensurate transition temperature T_I and that the incommensurate phase actually consists of large almost commensurate regions separated by narrow domain walls or "discommensurations" where the phase of the order parameter changes rapidly. The density n_s of these domain walls or phase solitons should go—according to the classical theory[1-3]—continuously to zero, $n_s \propto -\ln^{-1}(T - T_c)/T_c$, when the low-temperature commensurate (C) phase is approached, $T \to T_c^+$.

Renormalization-group calculations have, however, shown[4,5] that the influence of lattice dimensionality d on the critical behavior of the I-C transition is less pronounced than the influence of the dimensionality of the incommensurate modulation, m. For a $d = 2 + \epsilon$ dimensional system exhibiting a one-dimensionally modulated structure ($m = 1$), there is always a nonclassical critical region[5] for finite temperatures where the soliton density vanishes as $n_s \propto (T - T_c)^{1/2}$, which differs strongly from the classical result.[1-3] This discrepancy has not yet been checked experimentally.

Another important unsolved question is whether phase solitons are broad or narrow as compared to the lattice spacing. For narrow solitons the continuum approximation—used in most of the above theoretical treatments—is not applicable and the discreteness of the crystal lattice will lead to soliton pinning at particular lattice sites. The intersoliton distance will be an integral multiple of the lattice spacing leading to a series of commensurate structures[6] (the devil's staircase).

Quantitative experimental information on phase solitons in incommensurate systems in general —and structurally incommensurate systems in particular—is rather scarce. Evidence for the existence of phase solitons has been so far derived from (i) the presence of higher harmonics in the neutron-scattering diffraction pattern,[7] (ii) the existence of "sharp" lines in the ^{35}Cl nuclear-quadrupole-resonance (NQR)[8,9] and ^{87}Rb nuclear-magnetic-resonance (NMR)[10,11] spectra, and (iii) ^{77}Se NMR[12] line-shape measurements in the charge-density-wave (CDW) compound $2H$-$TaSe_2$.

In this Letter we report a quantitative determination of the variation of the soliton density n_s (defined as the ratio between the number of nuclei in the incommensurate domain walls and the total number of nuclei) with temperature in one-dimensionally modulated ($m = 1$) structurally incommensurate ($d = 3$) systems using NMR and EPR. The investigated systems are Rb_2ZnBr_4 (Ref. 13) and Rb_2ZnCl_4 (Ref. 14) (via ^{87}Rb quadrupole perturbed NMR) and γ-irradiated K_2SeO_4 (Ref. 15) [via electron paramagnetic resonance (EPR) of the SeO_4^{4-} centers]. Our data clearly show the presence of commensurate domains and incommensurate domain walls in the above structurally incommensurate systems, similar to what was done for incommensurate CDW systems in Ref. 12. Contrary to the case of $2H$-$TaSe_2$ (Ref. 12) the soliton width is found to be large as compared to the

intersoliton spacing over most of the I phase. The temperature variation of the soliton density close to T_c yields a nonclassical critical exponent $\frac{1}{2}$.

The study of incommensurate systems by magnetic resonance[10-12] is based on the fact that the NMR or EPR frequency is a function of the order parameter and thus varies in space in the I phase in a way which reflects the spatial variation of the incommensurate modulation. Since the translational lattice periodicity is lost, there is an essentially infinite number of nuclei or paramagnetic centers which contribute to the magnetic resonance spectrum. Except in the narrow soliton limit one thus expects to see a distribution of NMR or EPR frequencies which is quasicontinuous.

The density of spectral lines at the frequency ν will be given by

$$f(\nu) = N|d\nu/dx|^{-1}, \quad (1)$$

where N is the number of paramagnetic sites per unit length. Expanding ν in powers of the order parameter η as $\nu = \nu_0 + a_1\eta + \frac{1}{2}a_2\eta^2 + \cdots$ and taking into account that the order parameter is determined by its amplitude A and its phase φ, $\eta = A\cos\varphi(x)$, one finds $\nu = \nu_0 + \nu_1\cos\varphi(x) + \frac{1}{2}\nu_2 \times \cos^2\varphi(x) + \cdots$. The derivative appearing in Eq. (1) is thus given by

$$d\nu/dx = -(\nu_1 + \nu_2\cos\varphi + \nu_3\cos^2\varphi + \cdots) \times \sin\varphi\, d\varphi/dx, \quad (2)$$

where $\cos\varphi$ takes on nearly continuously all values between -1 and $+1$ and the coefficients $\nu_1 = a_1A$, $\nu_2 = a_2A^2$, $\nu_3, \ldots$ depend on the nuclear-site symmetry, the orientation of the magnetic field with respect to the symmetry elements of the crystal lattice, and temperature.

The spectral density $f(\nu)$ will be peaked whenever $d\nu/dx$ becomes small. In the "plane-wave" limit the phase φ is a linear function of x and the quasicontinuous function $f(\nu)$ will be peaked when $\sin\varphi = 0$ or when $\nu_1 + \nu_2\cos\varphi + \nu_3\cos^2\varphi + \ldots$ will be zero. In the soliton limit φ is a nonlinear function of x and one expects to see additional "commensurate" lines—occurring when $d\varphi/dx = 0$—superimposed on the incommensurate background. On going to the commensurate phase, $\cos\varphi$ takes on discrete values and only the "commensurate" lines remain.

The spatial variation of the phase $\varphi = \varphi(x)$ is obtained as a solution of the sine-Gordon equation

$$d^2\varphi/dx^2 = \alpha\sin(p\varphi), \quad (3)$$

which admits both plane-wave–like, as well as multisoliton latticelike solutions. The sine-Gordon equation can be reduced to a pendulumlike equation and numerically integrated on a computer to synthesize NMR or EPR line shapes $F(\nu)$ with the help of Eqs. (1) and (2) and the convolution

$$F(\nu) = \int L(\nu - \nu_c) f(\nu_c) d\nu_c, \quad (4)$$

where $L(\nu - \nu_c)$ is the line shape of a single spectral component.

Figure 1 shows the effect of soliton broadening on the line shape for $\varphi_0 = 0$, $p = 3$,[6-8] and $\nu_1 \neq 0$, $\nu_2 = \nu_3 = 0$ for various values of the parameter Δ, which is related to the relative volume fraction of the "commensurate" regions, $n_c = 1 - n_s$, in the inset. It is seen that for small Δ, i.e., narrow solitons, we have three peaks at $(\nu - \nu_0)/\nu_1 = -1$, -0.5, and 1. When the solitons broaden, the peak at -0.5 smears out. This is exactly the situation observed in the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectrum of Rb_2ZnCl_4 close to T_c.

From the temperature dependence of the intensities of the disappearing lines, the temperature

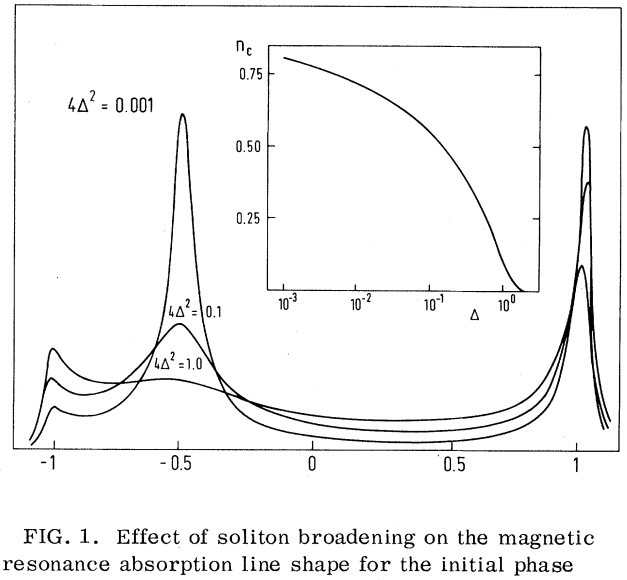

FIG. 1. Effect of soliton broadening on the magnetic resonance absorption line shape for the initial phase $\varphi_0 = 0$ and $p = 3$ (Refs. 6–8). Only the first-order term (ν_1) in the expansion of the frequency in terms of the order parameter is taken into account. The single-component line shape $L(\nu - \nu_c)$ was assumed to be Lorentzian with a half-width $\gamma = 0.03\ \nu_1$. The inset shows the relation between the parameter Δ and the relative volume fraction of the nearly commensurate regions n_c.

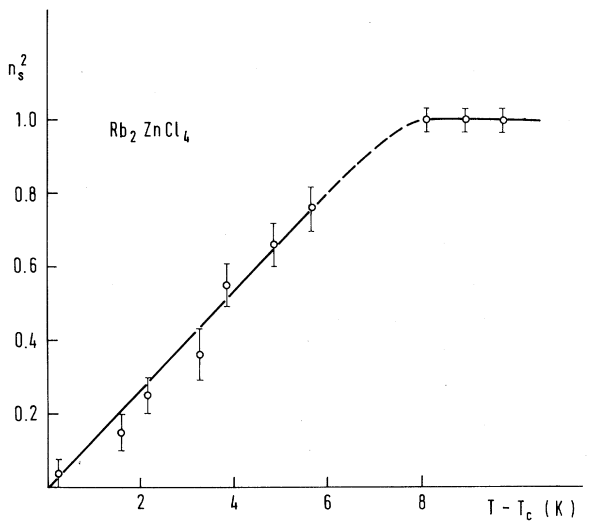

FIG. 2. Temperature dependence of the square of the soliton density in Rb_2ZnCl_4 as deduced from the ^{87}Rb NMR spectra on heating. The cooling run gave a similar curve with a small hysteresis (~ 1 K) in T_c.

variation of the soliton density $n_s = 1 - n_c$ has been determined (Fig. 2). The data can be fitted to a power law $n_s \propto (T - T_c)^{1/2}$ with a nonclassical exponent $\frac{1}{2}$ differing significantly from the classical result. The accuracy of the n_s data is not very high but is clearly sufficient to discriminate between the classical logarithmic and nonclassical power-law behaviors.

The temperature variation of the splitting between the two edge singularities $\Delta\nu \propto (T_I - T)^{\beta_A}$ further allows the determination of the temperature dependence of the amplitude A of the incommensurate order parameter. For both Rb_2ZnCl_4 and Rb_2ZnBr_4 one obtains a critical exponent $\beta_A = 0.36 \pm 0.02$ which agrees with the $d = 3$, $n = 2$ Heisenberg model (Fig. 3). The whole I phase is thus indeed critical in these $d = 3$, $m = 1$ systems.

It should be noted that the apparent mean-field value $\beta_A = \frac{1}{2}$ quoted in our first report[10] was due to the fact that, at the given orientation of the magnetic field, in addition to the linear term (ν_1) higher-order terms (ν_2 and ν_3) also influenced the splitting.

The observed ^{87}Rb NMR line shape in Rb_2ZnCl_4 and Rb_2ZnBr_4 as well as the EPR line shapes of the SeO_4^{4-} centers in K_2SeO_4 are, over most of the I phase, compatible with the broad-soliton picture where the soliton width is large as compared to the intersoliton spacing. This agrees with the fact[10,11] that the ^{87}Rb spin-lattice relaxation rate is determined by phasons in the I phase of both Rb_2ZnCl_4 and Rb_2ZnBr_4. The results definitely exclude the presence of narrow solitons except very close to the incommensurate-commensurate transition temperature T_c. The comparison between the experimental and calculated line shapes for one of the SeO_4^{4-} Q-band EPR lines in γ-irradiated K_2SeO_4 similarly demonstrates[16] that the relative volume fraction of the nearly commensurate regions is only $n_c = 0.01$ in the middle of the I phase at 110 K corresponding to a phase soliton density $n_s = 0.99$. The plane-

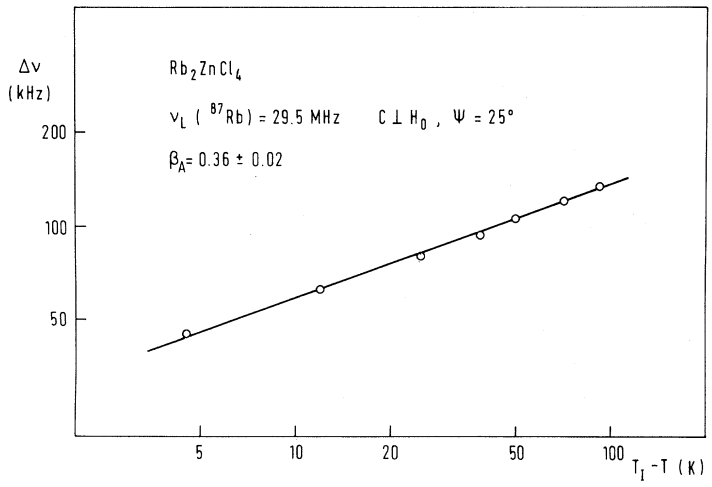

FIG. 3. Temperature variation of the splitting between the two edge singularities in the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra of Rb_2ZnCl_4.

wave modulation model—which corresponds to $n_c \to 0$—is thus here a good approximation for a large part of the I phase.

[a]On leave of absence from the Demokritos Nuclear Research Center, Athens, Greece.

[b]On leave of absence from the L. V. Kirensky Institute of Physics, Krasnoyarsk, U.S.S.R.

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Tricritical Points in the Equilibrium Polymerization of Sulfur Solutions

John C. Wheeler

Department of Chemistry, University of California–San Diego, La Jolla, California 92093

and

Pierre Pfeuty

Laboratoire de Physique des Solides, Associé au Centre National de la Recherche Scientifique, Université de Paris–Sud, Centre d'Orsay, F-91405 Orsay, France

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A dilute $n \to 0$ vector model provides a useful description of equilibrium polymerization in a solvent. Such polymerization occurs in liquid sulfur solutions and leads to a lower critical solution point that is analogous to the tricritical point found in ^{3}He-^{4}He mixtures. In the mean-field approximation, the model is identical to an earlier theory of Scott. Nonclassical critical behavior can explain certain discrepancies between Scott's theory and experiment.

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Recently we have shown[1,2] that equilibrium polymerization can be described by the $n \to 0$ limit of the n-vector model of magnetism in a small magnetic field, and that evidence for the nonclassical critical behavior of the $n \to 0$ vector model can be seen in the polymerization of liquid sulfur. In the molecular-field approximation, the $n \to 0$ vector model becomes identical[2] with the Tobolsky-Eisenberg[3] theory of equilibrium polymerization.

Solutions of liquid sulfur with a variety of organic solvents are unusual[4-6] in that they exhibit a temperature range of complete miscibility of the components, bounded below by the familiar upper critical solution temperature (UCST), T_1, and low-temperature phase separation, and bounded above by a lower critical solution temperature (LCST), T_2, above which the components again undergo phase separation. Scott[4] has presented a theory of these solutions based on the Flory-Huggins[7] theory of polymers and the Tobolsky-Eisenberg[3] theory of polymerization, and has shown that it is capable of reproducing many of the quali-

