Evidence for a 1-*q* to 3-*q* Transition and 3-*q* Soliton Lattice in Incommensurate Proustite

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^{75}As nuclear quadrupole resonance line shape data demonstrate the existence of a transition from a single-q state, consisting of a superposition of one dimensionally modulated incommensurate domains, to a genuine triple-q modulated incommensurate state with three independent noncoplanar modulation waves in the high temperature part of the incommensurate phase of proustite. The NMR spectra are consistent with the existence of a triple-q modulated multisoliton lattice in the low temperature part of the incommensurate phase. The temperature dependence of the soliton density has been determined. [S0031-9007(98)05523-9]

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In incommensurate (I) systems the periodicity of at least one of the modulation waves cannot be expressed as a rational frequency of the periodicity of the underlying lattice [1–3]. As a result of that the translational lattice periodicity is lost in spite of the existence of perfect long range order. Phase transitions leading to such I phases are described by order parameters with a minimum dimensionally two ($n = 2$), four ($n = 4$), or six ($n = 6$) resulting in systems with one (1-q), two (2-q), and three (3-q) incommensurate modulation waves.

The modulation waves are independent if the modulation vectors $\vec{q}$ are independent and the corresponding phases are not correlated. If, however, the number of modulation waves is larger than the dimension D of the space spanned by the corresponding wave vectors and their phases are correlated, the modulation waves are not independent. The properties of such a system now strongly depend on the relative phases of the modulation waves. Such a situation occurs, for example, in quartz (see review by Dolino in Ref. [3]) and berlinite [4] where $n = 6$, but the three modulation waves are coplanar, $D = 2$, $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0$, and their relative phase is fixed, $\Psi_1 + \Psi_2 + \Psi_3 = \Psi = 0$, $\pm\pi/2$ or π, as well as in several charge density wave (CDW) systems, e.g., in 2H-$TaSe_2$ [5–7]. It should be stressed that the properties of the above 3-q, $D = 2$ systems should be qualitatively different from those of a noncoplanar 3-q, $D = 3$ I system with three independent modulation waves.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are ideally suited for a determination of the number of independent modulation waves in I systems, as well as the determination of their relative phases if the modulation waves are correlated (Fig. 1). Here we report on the discovery of a 1-q to 3-q transition in incommensurate proustite by ^{75}As NQR, as well as on the first observation of solitons in a nonplanar 3-q modulated I system with $n = 6$, $D = 3$. Our line shape data demonstrate that we deal in the low temperature part of the I phase in proustite with three independent noncoplanar incommensurate modulation waves and not with the superposition of 1-q domains with different orientations of q vectors. Proustite thus represents so far the only known example of a genuine three dimensional I system with three independent incommensurate modulation waves. Solitons have been observed in 1-q insulators [3,8,9] and in a number of coplanar 3-q CDW systems, e.g., in 2H-$TaSe_2$ by NMR [5], x-ray [6], and scanning tunneling microscopy [7], but not in any noncoplanar 3-q case.

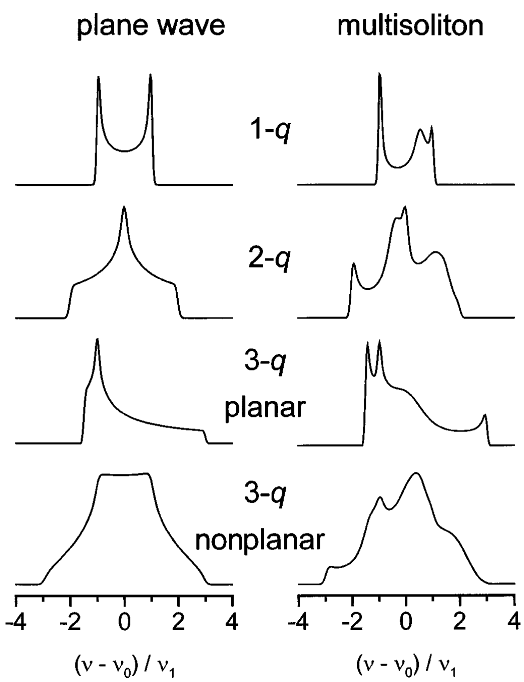

FIG. 1. Theoretical NQR line shapes for the 1-q, 2-q, planar 3-q, and nonplanar 3-q incommensurately modulated systems in the plane wave and multisoliton lattice limits for a linear relation between the resonance frequency and nuclear displacement. The line shapes are obtained from Eq. (5). For the soliton limit the phases are obtained as solutions of the sine-Gordon equation (7). In the planar 3-q case the position of the central logarithmic singularity depends on the relative phases of the modulation waves, even in the plane wave limit, while in this limit the spectrum is independent of the initial phases for the noncoplanar 3-q case.

Proustite, Ag_3AsS_3, belongs at room temperature to the space group $R3c(C_{3v}^6)$ with two formula units per primitive unit cell [11]. The AsS_3 pyramids occupy the C_3 sites and the two As nuclei in the unit cell are chemically equivalent. X-ray studies [12,13] have shown that the I phase in proustite [14,15] below $T_I = 60$ K is, in fact, triple-q modulated and that the q vectors are in contrast to quartz noncoplanar. On the basis of x rays it is, however, hard to discriminate between a superposition of 1-q domains with different orientations of q vectors and a genuine 3-q modulated state. The theory of Pokrovsky [10] predicts that both of these possibilities could exist in proustite below T_I.

The I state in proustite can be described by a six component order parameter [10]

$$Q_{\pm i} = \rho_i \exp[\pm i\Phi_i(\vec{x}_i)], \qquad i = 1,2,3, \tag{1}$$

where ρ_i stands for the amplitude and Φ_i for the phase of the three independent incommensurate modulation waves. If the 1-q multidomain state is realized below T_I, then for a given domain one of the following possibilities is realized:

$$\begin{aligned} &\text{(i) } \rho_1 = \rho_2 = 0, \qquad \rho_3 \neq 0, \\ &\text{(ii) } \rho_2 = \rho_3 = 0, \qquad \rho_1 \neq 0, \text{ or} \\ &\text{(iii) } \rho_3 = \rho_1 = 0, \qquad \rho_2 \neq 0. \end{aligned} \tag{2a}$$

Each domain is modulated here in a single direction, but the direction of the modulation wave vector varies from one domain to another. For the genuine 3-q state we have, on the other hand, a simultaneous incommensurate modulation along three different directions

$$\rho_1 = \rho_2 = \rho_3 = \rho \neq 0. \tag{2b}$$

In the general case, the dependence of the NQR resonance frequency ν_i on the nuclear displacements u_i in the I phase is nonlocal

$$\nu_i = \nu[u_i(x_i), u_j(x_j), \ldots], \qquad i \neq j, \tag{3}$$

where j runs over all ions that contribute to the resonance frequency at the ith site. Expanding the above relation in powers of the displacements one finds for the ^{75}As NQR frequency in proustite in the 3-q case

$$\nu_i(\Phi_1,\Phi_2,\Phi_3) = \nu_0 + \nu_1 \sum_{i=1}^{3} \cos(\Phi_i) + \nu_2 \sum_{i=1}^{3} \cos(2\Phi_i + \Phi_{20}) + \cdots, \tag{4}$$

where ν_1 is proportional to the amplitude of the modulation wave $\nu_1 \propto \rho \propto (T - T)^\beta$, i.e., to the order parameter, and $\nu_2 \propto (T - T)^{\tilde{\beta}}$ with $\tilde{\beta} \simeq 2\beta$. Φ_{20} describes the relative phase shift between the linear and quadratic terms. The incommensurate frequency distribution f_{3q} is now obtained [16] in the constant amplitude approximation as

$$f_{3q}(\nu) = K \int\int\int \delta\{\nu - \nu[\Phi_1(x_1), \Phi_2(x_2), \Phi_3(x_3)]\} \times dx_1\, dx_2\, dx_3, \tag{5}$$

where the x_i are variables along the directions of the modulation wave vectors [10]. In the 1-q case expansion (5) simplifies to the well known expression [3]

$$f_{1q}(\nu) = K \int \delta\{\nu - \nu[\Phi_1(x_1)]\}\, dx_1 = \frac{\text{const}}{d\nu/dx_1} = \frac{\text{const}}{(d\nu/d\Phi_1)\,(d\Phi_1/dx_1)}. \tag{6}$$

The resulting line shapes for 1-q, 2-q, planar 3-q, and noncoplanar 3-q cases are shown in Fig. 1 for the plane wave, as well as for the multisoliton lattice limits. In the linear case ($\nu_2 = 0$) one thus finds for a 1-q plane wave-type modulation a frequency distribution limited by two edge singularities at $\nu - \nu_0 = \pm\nu_1$, where $d\nu/d\Phi_1 = 0$ (Fig. 1). In the 2-q case we find a line shape, characterized by a logarithmic singularity in the center. For the planar 3-q case the line shape is similar to that of the 2-q case, but the position of the central singularity depends on the relative phases between the modulation waves. For the noncoplanar 3-q phase with three independent modulation waves the NMR spectrum is bell shaped and does not depend on the initial phases in the plane wave limit. As long as Φ_1 is a linear function of x_1, $d\Phi_1/dx_1$ is nonzero and constant, and this term does not affect the spectral line shape. In the nonlinear case of a multisoliton lattice, on the other hand, $d\Phi_1/dx_1 \to 0$ in the commensurate regions leading to the appearance of the characteristic "commensurate" lines [8] in the spectrum.

From the Landau-type free energy expansion model of Pokrovsky [10], one finds that in the simplest case, the independent phases of the three modulation waves are obtained as solutions of the three uncoupled sine-Gordon equations

$$\Phi''(x_i) = -6Dt^2 \sin[6\Phi(x_i)], \qquad i = 1,2,3. \tag{7}$$

Here $t = 1 - T/T_C$ and D is a constant dependent on the parameters of the Landau free energy expansion first derived for proustite by Pokrovsky [10]. The solutions for Φ_i are elliptic amplitudes as in the 1-q case. The multisoliton line shapes in Fig. 1 are now obtained by inserting solutions of Eq. (7) into Eq. (5).

We have studied the I phase of an optically pure proustite single crystal by ^{75}As NQR spectroscopy. The width of the NQR spectrum changes from 10 kHz in the normal phase to $\approx$1.1 MHz in the lower part of the I phase [14]. The spectrum was measured by the "point-by-point" method with automatic tuning of the resonant circuit at each frequency. At each frequency the spectral intensity was obtained by integrating the Fourier transform of the quadrupolar echo following a

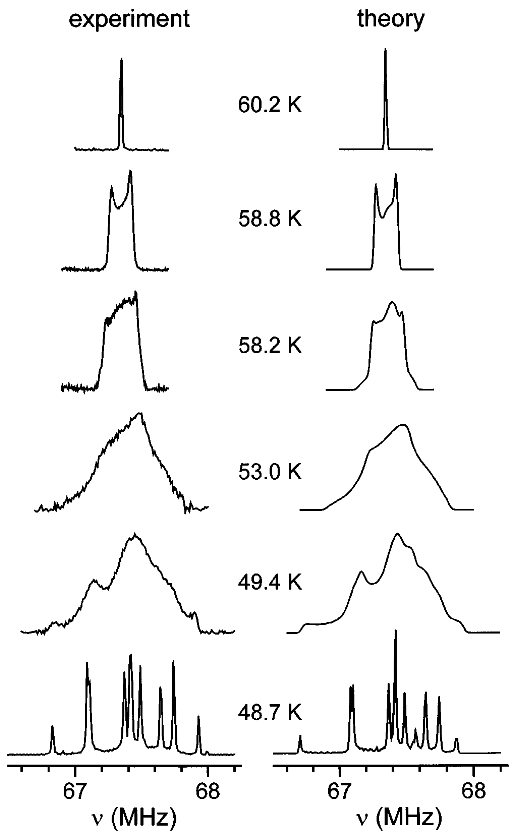

FIG. 2. Comparison between the observed and theoretical ^{75}As NQR line shapes in proustite: (a) $T = 60.2$ K, paraphase; (b) $T = 58.8$ K, 1-q incommensurate phase; (c) $T = 58.2$ K, coexistence of 1-q and 3-q phases; (d) $T = 53.0$ K, plane wave regime of 3-q incommensurate phase; (e) $T = 49.4$ K, multisoliton regime of 3-q incommensurate phase; and (f) $T = 48.7$ K, commensurate phase C_1.

$\pi/2 - \pi$ pulse sequence. The typical frequency step was 5 kHz. The temperature stability was ± 0.02 K.

On cooling into the I phase the NQR spectrum becomes inhomogeneously broadened (Fig. 2). The line shape with two edge singularities observed just below T_I at 58.8 K is typical for a 1-q modulated system in the plane wave limit. On further cooling into the I phase an asymmetrical bell-like spectral component appears which gradually replaces the 1-q spectrum. This component, which dominates the spectrum already 2 K below T_I, is typical of a 3-q modulated system. We have thus observed a transition from a state, characterized by a superposition of 1-q domains—Eq. (2a)—with different directions of modulation vectors to a genuine 3-q state—Eq. (2b)—where the crystal is simultaneously modulated along three different directions.

As shown in Fig. 3(b)—where the Pokrovsky-type [10] free energies of these two phases are compared—the 1-q solution is stable in the high T part of the I phase, whereas the 3-q solution is stable at lower temperatures. This has been indeed observed. From the 1-q fit we also obtain the critical exponent for the amplitude of order parameter $\beta_{1q} = 0.3 \pm 0.02$, $\tilde{\beta}_{1q} \approx 2\beta_{1q} = 0.6 \pm 0.02$, and $\Phi_{20} = 80°$. The analogous parameters for the 3-q phase are $\beta_{3q} = 0.4 \pm 0.02$, $\tilde{\beta}_{3q} = 2\beta_{3q} = 0.8 \pm 0.02$, and $\Phi_{20} = 50°$.

Between 57.5 K and 52 K the NQR line shape is essentially the one expected for the 3-q case in the plane wave modulation limit (Fig. 2). The nonlocal 3-q simulation gives an almost perfect fit between the theoretical and the experimentally observed line shape. The comparison of the ^{75}As NQR line shape of proustite (3-$q, D = 3$) and the ^{27}Al NMR line shape in berlinite (3-$q, D = 2$) [4] (Fig. 1) further demonstrates the power of NMR and NQR line shape measurements in determining the number of independent modulation waves and the dimension of the space spanned by the corresponding wave vectors.

Below 52 K the spectrum becomes structured indicating the formation of a 3-q multisoliton lattice (Fig. 2) where the phases of the modulation waves are nonlinear functions of the spatial coordinates. From a comparison of experimental and theoretical line shapes—Eq. (3)—we have determined with the help of the

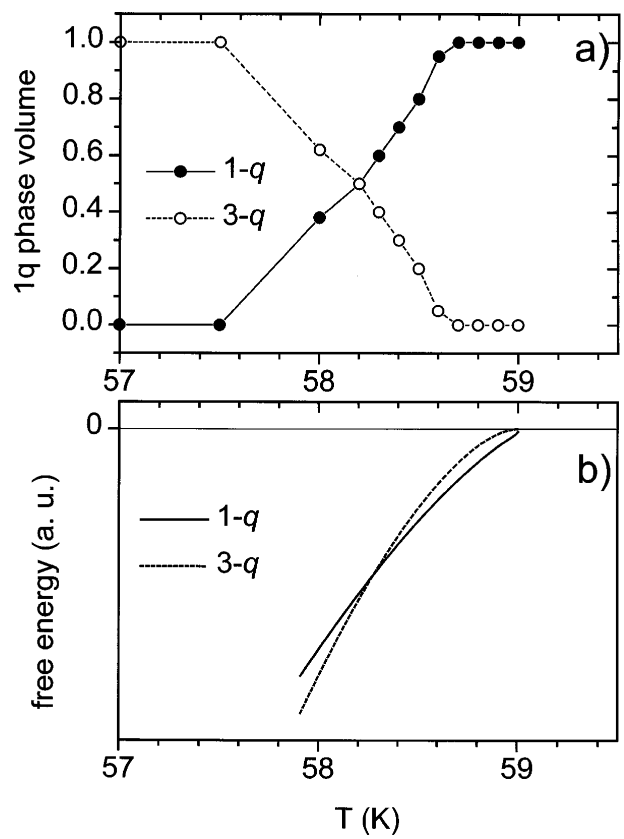

FIG. 3. (a) Temperature dependence of the volume fraction of the 1-q and 3-q phases of proustite. (b) Temperature dependence of the free energies of the 1-q and 3-q phases of proustite calculated on the basis of Pokrovsky model [12]. We kept the sixth order invariants independent of the phases $E_1 \sum_i |\eta_i|^6$, $E_2(\sum_i |\eta_i|^4)(\sum_i |\eta_i|^2)$, and $E_3(\sum_i |\eta_i|^2)^3$ that were omitted in Eq. (2) in Ref. [12]. The values of the relevant coefficients (using Pokrovsky's notation) chosen here are $C_1/B = -2$, $C_2/B = 0$, $E_1/B = 2$, $E_2/B = 0$, and $E_3/B = 2$.

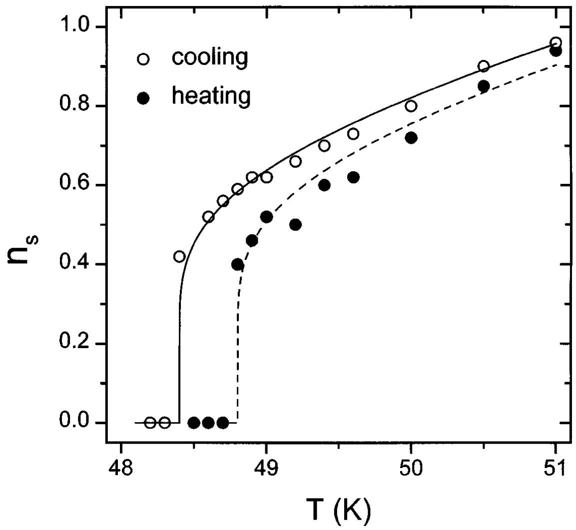

FIG. 4. Temperature dependence of the soliton density n_{si} in proustite. The solid line shows the theoretical prediction from expression (8).

first integral of the sine-Gordon [1–3,8] equations (7) the soliton density $\eta_{si} = d_i/l_{ci}$ for each of the three modulation waves. The initial phases were chosen to optimize the fit, as well as to give the proper positions of the commensurate lines in the C phase (Fig. 2). The fit is therefore unique. In the expression for the soliton density $n_{si} = d_i/l_{ci}$, d_i is the width of the phase soliton and l_{ci} the intersoliton distance which diverges on approaching the incommensurate-commensurate (I-C) transition at T_C. In view of the point group symmetry we have $\Phi_1 = \Phi_2 = \Phi_3$ and $n_s = n_{s1} = n_{s2} = n_{s3}$. The temperature dependence of the soliton density n_{si} on approaching T_C is shown in Fig. 4. It can be relatively well described by the Pokrovsky [10] model which in the simplest approximation predicts

$$n_{si} = \frac{\pi/2}{K(k)} \propto -\frac{1}{\ln[(T - T_C)/T_C]}, \qquad i = 1, 2, 3, \tag{8}$$

where $K(k)$ is a complete elliptic integral of the first kind. Here k, which depends on the amplitude of the modulation wave, is determined [1–3] by a minimization of the free energy. The constant k is also directly related to the spatial derivative of the phase of the modulation wave $d\Phi_i/dx_i$ and is thus experimentally accessible via NMR and NQR line shape measurements.

At the I-C transition all three n_{si} vanish and the incommensurate frequency distribution is replaced by a multiplet of narrow lines reflecting the multiplication of the unit cell. Here the phases of three modulation waves Φ_i are step functions, taking the commensurate values $\vartheta_1 = \pi/3$, $\vartheta_2 = \pi$, and $\vartheta_3 = 5\pi/3$. For every combination of commensurate values of phases $\Phi_1(\vec{r}) = \vartheta_i$, $\Phi_2(\vec{r}) = \vartheta_j$, $\Phi_3(\vec{r}) = \vartheta_k$ there is a corresponding peak in the NQR spectrum at frequency $\nu(\vartheta_i, \vartheta_j, \vartheta_k)$. The single resonant line of the high temperature phase should be, therefore, replaced by $3^3 = 27$ lines. Since, however, ν_{3q} is invariant to the permutation of the phases ϑ_i, ϑ_j, and ϑ_k, many lines in the C_1 phase overlap. The intensity of the resonance lines is proportional to the number of permutations of phases corresponding to a given frequency. The As NQR spectrum below T_C should thus consist of three lines with a relative intensity 1, six lines with a relative intensity 3, and a single line with a relative intensity 6. This agrees rather well with the observed spectrum (Fig. 2). The hysteresis of 0.6 K, observed at the I-C transition agrees with measurements from Ryan *et al.* [12] and seems to be due to the pinning of the soliton lattice to defects.

In summary, we have performed the first study of phase transitions inside the I phase and of the temperature dependence of the soliton density for a $D = 3$, $n = 6$ incommensurate system with three noncoplanar modulation waves. All other 3-q modulated systems where soliton lattices have been studied so far have three coplanar modulation waves. We have found a 1-q to 3-q transition in the high-temperature part of the I phase of proustite and have shown that we deal in the low temperature part of the I phase with a genuine triple-q modulated I phase with three independent modulation waves and not with a superposition of 1-q domains with different orientations of wave vectors.

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