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New Type of Soliton Solutions from a Landau Potential Describing the β-γ-δ-Transitions in $(C_3H_7NH_3)_2MnCl_4$

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Abstract: The incommensurate γ-phase of the perovskite-type layer structure compound $(C_3H_7NH_3)_2MnCl_4$ is sandwiched between two phases (β, δ) which have the same structure. The Landau potential describing this behaviour reveals besides the plane-wave solution also a new type of soliton solutions which differ from the solutions of the sine-Gordon equation.

Introduction

Perovskite-type layer structures of the formula $(C_nH_{2n+1}NH_3)_2MCl_4$ with short hydrocarbon chains (n<5) are known to exhibit several structural phase transitions which are connected with reorientational jumps of the alkylammonium chains /1/. Within this family the compound $(C_3H_7NH_3)_2MnCl_4$ is a special case because of its complicated phase sequence with two incommensurate phases /2,3/. The different phases are denoted as α, β, γ, δ, ε and ζ.

$P2_1/n$	Inc.	Abma	Inc.	Abma	I4/mm
Z=6	$\vec{q} \simeq \frac{1}{3}\vec{b}^*$	Z=4	$\vec{q} \simeq \frac{1}{6}\vec{a}^* + \vec{c}^*$	Z=4	Z=2
ζ	ε	δ	γ	β	α
	110 K	165 K	344 K	396 K	443 K → T

The most interesting feature is the reentrant behaviour of the γ-δ-transition. It was shown by means of NMR-NQR that the β and the γ-phase have indeed the same structure /4/. They differ only in the saturation of the order parameter of the α-β-transition. This reentrant behaviour could be well described by a

Landau-type free energy /4/. It was shown that a plane wave modulation is an exact solution of the corresponding Euler equations. In this contribution we want to stress also soliton-like solutions in order to explain the observed types of x-ray satellite reflections.

Incommensurate Wave Vectors of the γ-Phase

An x-ray analysis of the γ-phase revealed three types of satellite reflections /2/:

type A1: $\vec{q}_1=\alpha\vec{a}^*+\vec{c}^*$, $\alpha\simeq 0.17$, strong *)

A2: $\vec{q}_2=2\alpha\vec{a}^*$, weak

B : $\vec{q}_3=\beta\vec{a}^*+\vec{c}^*$, $\beta\simeq 0.05$, weak

$\vec{q}_1$ and $\vec{q}_3$ are zone-boundary vectors on the H line near the Y point, $\vec{q}_2$ is on the Λ line (notation according to ref.5). The type A2 satellites are obviously due to a higher harmonic of the type A1 modulation and are generated by a third-order anharmonic potential $V_3(Q^2_{q_1}Q_{-q_2}+Q^2_{-q_1}Q_{q_2})$. The origin of the B-type modulation is still an open question.

The commensurate part of the modulation ($=\vec{c}^*$) destroys the A-centering of the unit cell. The superspace group compatible with the A1 reflections is $N^{A\bar{b}ma}_{\ 111}$ /2/. The soft mode leading to this superspace group must transform according to the irreducible representation H_1, which splits at the Y point into the one-dimensional representations Y_1^+ and Y_3^- having at the Γ point x^2 and x symmetry respectively. At the Y point there is no degeneracy of modes and therefore no Lifshitz invariant is allowed. At the other end of the H line, at the T point $(\frac{1}{2}\vec{a}^*+\vec{c}^*)$, all modes are doubly degenerate and Lifshitz invariants can be formed. The mode softening with a wave vector close to the Y point is in our case due to a coupling of two modes with Y_1^+ and Y_3^- symmetry.

*) $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$ are given for the A-centered unit cell .

Thermodynamic Potential and Discussion of the Euler Equations

A free energy explaining the reentrant behaviour of the γ-δ-transition is given in ref.4. A coupling of the order parameter with the density of the layers leads to renormalized Landau coefficients $\hat{A}(T)$ and $\tilde{B}(T)$ containing both linear and quadratic terms in $(T-T_o)$. Outside the γ-phase the density of layers must exhibit a linear term in the temperature dependence to provide the reentrant behaviour. The free energy density is thus given by:

$$g = g_o + \frac{1}{2}\hat{A}\eta\eta^* + \frac{1}{4}\hat{B}(\eta\eta^*)^2 - \frac{1}{2}\kappa\frac{d\eta}{dx}\frac{d\eta^*}{dx} + \frac{1}{2}\lambda\frac{d^2\eta}{dx^2}\frac{d^2\eta^*}{dx^2}, \quad \kappa,\lambda > 0$$

The plane wave $\eta = Ae^{iq_0x}$ (A=const., $q_0^2 = \kappa/2\lambda$) is an exact solution of the resulting Euler equations. A more general solution can be obtained within a constant-amplitude approximation ($\eta = Ae^{i\Phi(x)}$, A=const.). In this case Φ can be expressed in terms of elliptic integrals of the first kind. Introducing the function $h = \frac{1}{q_0^2}\cdot\left(\frac{d\Phi}{dx}\right)^2 - 1$ the Euler equation for the phase Φ reads after one integration:

$$\left(\frac{dh}{dx}\right)^2 = 4q_0^2(h+1)(h^2-\mu^2) \qquad \mu: \text{ integration const.}$$

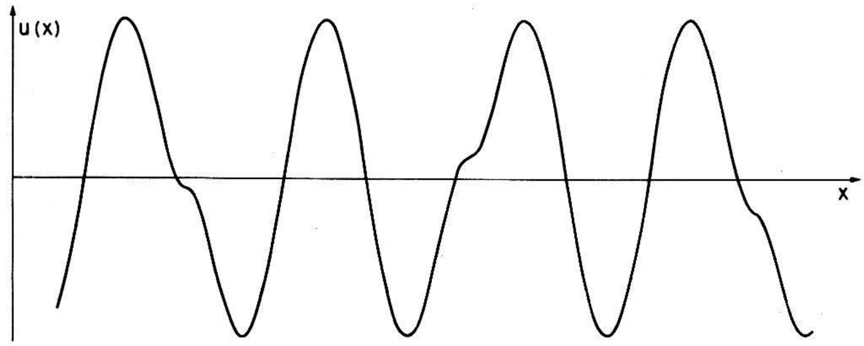

Fig. 1 Normalized atomic displacement $u(x)=\sin(\phi(x))$ for $k=\sin^{-1}(89^o)$.

The solution can be evaluated by the integral

$$x = \frac{1}{\sqrt{1+\mu}}\,\frac{1}{q_0}\int_0^{\varphi}\frac{d\psi}{\sqrt{1-k^2\sin^2\psi}}\ , \quad h = -1 + (1-\mu)\sin^2\varphi\ , \quad k^2 \equiv \frac{1-\mu}{1+\mu}$$

or written in a condensed form:

$$\phi = \int_0^x q_0\sqrt{1+h(x')}\,dx'\ , \quad h(x) = -1 + (1-\mu)\sin^2(\mathrm{sn}(q_0\sqrt{1+\mu}\,x))$$

In the plane-wave case, $h=0$, $\mu=0$ and $k=1$.

Some results are shown in Figures 1 and 2. In contrast to the solution of the sine-Gordon equation where only higher harmonics are obtained our equation leads also to "subharmonic" parts which would explain the B-type x-ray reflections.

By introducing h into the free energy $F=\int g\,dV$ one gets: $F = F_0 + V\left\{\frac{1}{2}\left[\hat{A} + \lambda q_0^4(-1+H(k))\right]A^2 + \frac{1}{4}\hat{B}A^4\right\}$

$$H(k) \equiv 2\langle h^2\rangle - \frac{1-k^2}{1+k^2}\ .$$

The average of h^2 is given by $\langle h^2\rangle = \int_0^{\pi/2}\frac{h^2(\varphi)\,d\varphi}{\sqrt{1-k^2\sin^2\varphi}}\Big/\int_0^{\pi/2}\frac{d\varphi}{\sqrt{1-k^2\sin^2\varphi}}$

The minimum of F with respect to k is obviously independent of A and coincides with the minimum of H(k). This function is shown in Fig.3. It can be seen that the plane-wave solution (k=1) has a lower free energy than a solution with a space-dependent $\frac{d\Phi}{dx}$. However, our free energy contains only the leading terms necessary to explain both, the incommensurability and the reentrant behaviour. A complete free-energy density up to the fourth order of

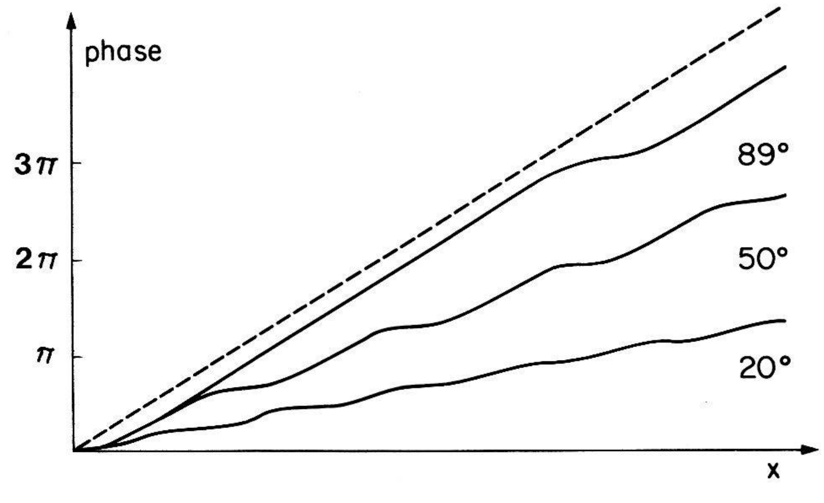

Fig. 2 Phase angle ϕ vs. x for different values of $\sin^{-1}(k)$. The dashed line corresponds to the plane-wave solution.

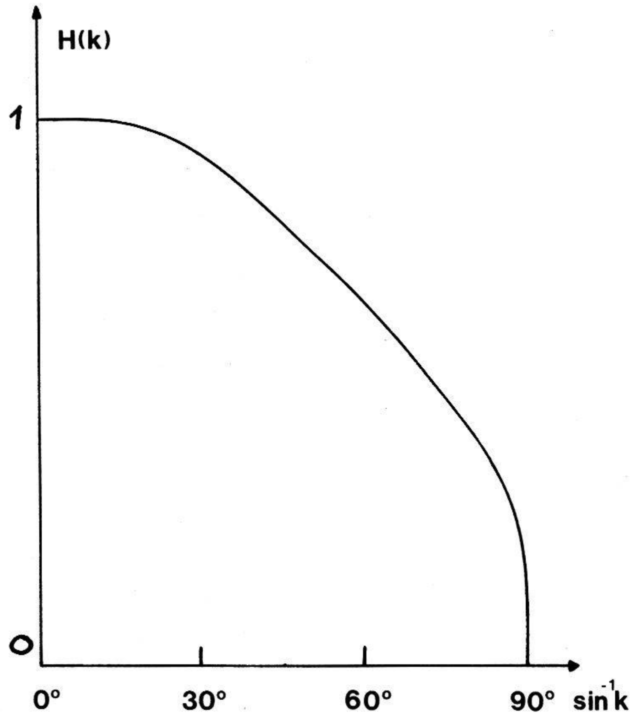

Fig. 3
The function H (as defined on the preceding page) vs. $\sin^{-1}(k)$.

the amplitude should also take into account the terms $\sigma(\frac{d\eta}{dx}\frac{d\eta^*}{dx})^2$ and $\rho(\frac{d^2\eta^*}{dx^2}\frac{d^2\eta}{dx^2})^2$. Especially the first of these terms with $\sigma>0$ would favour a solution with $k<1$, since with lower k the value of $\langle\frac{d\Phi}{dx}\rangle$ is reduced.

The effect of a space-dependent amplitude can not be predicted since it would require the solution of two coupled strongly non-linear Euler equations. It was shown/6/, however, that the amplitude variations do not play an essential part in modulated structures of the β-K_2SO_4 family.

To conclude we can say that our Landau potential doesn't only describe the reentrant behaviour but also explains all kinds of the observed x-ray satellites. The crucial experiment to test our theory should be the measurement of the temperature dependence of the splitting and the intensity of the B-type reflections.

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