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Incommensurate-Reentrant High-Symmetry Phase Transition in a Layer-Structure Perovskite

P. Muralt, R. Kind, and R. Blinc [a]

Laboratory of Solid State Physics, Swiss Federal Institute of Technology, Hönggerberg, CH-8093 Zürich, Switzerland

and

B. Zeks

J. Stefan Institute, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia

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In contrast to the usual structural "lock-in" incommensurate-commensurate transitions—where the amplitude of the modulation wave continues to increase at T_c but the incommensurate part of the average wave vector of the modulation wave vanishes—in $(C_3H_7NH_3)_2MnCl_4$ the amplitude of the incommensurate modulation wave vanishes outside T_{c1} and T_{c2} whereas the wave vector is not critical. This reentrant behavior results from a coupling of the incommensurate order parameter to the temperature-dependent interlayer distance.

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The phase-transition sequence commonly observed[1] in structurally incommensurate systems is as follows: high-temperature disordered phase (P)—incommensurately modulated ordered phase (I)—commensurate ordered phase (C). The P-I transition is the result of a condensation of a soft mode with a wave vector which is incommensurate to the periodicity of the underlying lattice, whereas at the I-C transition the frozen-out modulation wave becomes commensurate, i.e., the average wave vector "locks in" to the basic lattice. Here we report on a thermal dilatation-induced incommensurate-reentrant high-symmetry phase transition in normal and partially deuterated $(C_3H_7NH_3)_2MnCl_4$ (abbreviated as C3Mn) where the *amplitude* of the modulation wave and *not* the incommensurate part of the average wave vector vanishes (Fig. 1) with lowering temperature. This phenomenon has so far not been observed in other incommensurate systems.

C3Mn is a pseudo-two-dimensional perovskite where layers of corner-sharing $MnCl_6^-$ octahedra are sandwiched between rigid—but dynamically disordered—propylammonium chains.[2,3] In the high-temperature α phase (space group $I4/mmm$) the propylammonium groups are reorienting around their long axes between four equivalent orientations. In the partially ordered β phase the

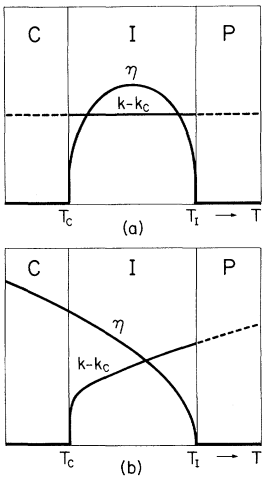

FIG. 1. Schematic temperature dependence of the amplitude (η) and the average incommensurate wave vector (k-k_c) in (a) C3Mn and (b) a "normal" incommensurate system in the P, I, and C phases.

orientations become nonequivalent, resulting in an average tilt of the C-N bond directions.

Whereas the atomic coordinates in the β phase have not yet been determined[2] our chlorine and deuteron quadrupole resonance studies[4] show, in addition to this tilt, a slight reorientation of the $MnCl_6^-$ octahedra around the b axis. The long molecular axes of the propylammonium groups are, however, still perpendicular to the $MnCl_4^-$ (i.e., a-b) planes.

In the incommensurate γ phase[5] which extends from 396 to 334 K the long molecular axes of the propylammonium groups are tilted[5,6] with respect to the normals to the a-b planes. The propylammonium tilt angles, the $MnCl_4^-$ layers, and the interlayer distance are modulated[5,6] (Fig. 2). The incommensurate wave vector is parallel to $\vec{a}$ and the modulation amplitude is parallel to $\vec{c}$, i.e., perpendicular to the $MnCl_4^-$ layer.[5] The modulation wavelength is about 40 Å and the amplitude ≈ 0.5 Å.[5] The incommensurate modulation vanishes[2] in the low-temperature δ phase (space group $Abma$, $z=4$). Depmier and co-workers[2] suggested that the β and δ phases might have the same space group so that the γ phase is embedded between two phases of the same symmetry.

Our chlorine and deuteron resonance measurements[4,6] show that this is indeed the case and that we are dealing in C3Mn with an incommensurate-reentrant high-symmetry phase transition. In this Letter we present the first direct observation of the temperature dependence of the amplitude of the order parameter for such a transition. We also show that within a Landau theory the incommensurate-reentrant high-symmetry phase transition results from a coupling of the incommensurate order parameter η—representing a modulated tilt angle of the propylammonium groups—to the interlayer distance d which represents a secondary, non-symmetry-breaking order parameter (Fig. 2). The conditions for the existence of the incommensurate phase are thus fulfilled only in a restricted temperature interval.

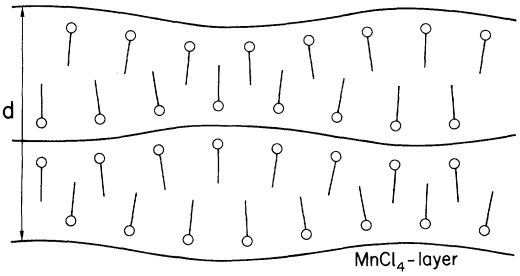

FIG. 2. Schematic structure of C3Mn showing the I modulation of the layers and the propylammonium-group tilt angles.

The part of the nonequilibrium free energy density involved in the $\beta \rightarrow \gamma \rightarrow \delta = \beta$ transitions can be expressed as

$$g = g_\eta + g_d + g_I , \tag{1}$$

where

$$g_\eta = \frac{1}{2} A \eta\eta^* + \frac{1}{4} B(\eta\eta^*)^2 - \frac{1}{2}\kappa \frac{d\eta}{dx}\frac{d\eta^*}{dx} + \frac{1}{2}\lambda \frac{d^2\eta}{dx^2}\frac{d^2\eta^*}{dx^2} \tag{2a}$$

with $A = a(T - T_0)$, $a, B, \kappa, \lambda > 0$;

$$g_d = C(T - T_0)(d - d_0) + \tfrac{1}{2} D(d - d_0)^2, \quad D > 0, \quad C > 0 ; \tag{2b}$$

and

$$g_I = E(d - d_0)\eta\eta^* + \tfrac{1}{2} F(d - d_0)^2 \eta\eta^* + E'(d - d_0)(\eta\eta^*)^2 + \tfrac{1}{2} F'(d - d_0)^2(\eta\eta^*)^2, \quad E, E' < 0, \quad F, F' > 0 . \tag{2c}$$

Here d_0 designates the distance d between two equivalent $MnCl_4^-$ layers (Fig. 2) of the less-ordered phase at T_0 and expression (2b) represents an expansion of g_d in powers of the small parameter $d - d_0$. The existence of a linear term in (2b) is due to the fact that $d - d_0$ is not a symmetry-breaking order parameter and is different from zero both above and below T_0. The linear temperature dependence of the interlayer distance d outside the incommensurate phase (i.e., represented by the term g_d) is the result of a coupling of d with the square of the order parameter η_2 of the β phase. No Lifshitz invariant in η is allowed by crystal symmetry at the Y point. The negative sign of the elastic κ term in (2a) is due to a coupling of the Y_1^+ mode with the Y_3^- mode outside the Y point on the H line parallel to a^*. This coupling results in a pseudo-Lifshitz-invariant term which is different from zero outside the Y point and which renormalizes κ. The interaction term g_I describes the fact that the modulated structure requires more space than the unmodulated one at a given temperature.

Minimizing g with respect to $d-d_0$,

$$(d-d_0)_0 = -\frac{C(T-T_0)+E|\eta|^2+E'|\eta|^4}{D+F|\eta|^2+F'|\eta|^4}, \tag{3}$$

substituting back into g, and expanding up to η^4, we find

$$g = g_0 + \frac{1}{2}\tilde{A}\eta\eta^* + \frac{1}{4}\tilde{B}(\eta\eta^*)^2 - \frac{1}{2}\kappa\frac{d\eta}{dx}\frac{d\eta^*}{dx} + \frac{1}{2}\lambda\frac{d^2\eta}{dx^2}\frac{d^2\eta^*}{dx^2}, \tag{4}$$

where

$$g_0 = -(C^2/2D)(T-T_0)^2, \tag{5a}$$

$$\tilde{A} = \tilde{a}(T-T_0) + (C^2F/D^2)(T-T_0)^2, \quad \tilde{a} = a - 2EC/D, \tag{5b}$$

$$\tilde{B} = B - \frac{2E^2}{D} + \frac{4C}{D}\left(\frac{EF}{D} - E'\right)(T-T_0) - \frac{2C^2}{D^2}\left(\frac{F^2}{D} - F'\right)(T-T_0)^2. \tag{5c}$$

The coupling of η with the temperature-dependent interlayer distance d thus results in a temperature dependence of the renormalized Landau expansion coefficients. In the following we shall assume that $\tilde{B}$ is always positive. Expanding $\eta(x)$ into a Fourier series, we get the harmonic part of the free energy $F^{(2)} = \int g\,dV$ as

$$F^{(2)} = F_0 + \tfrac{1}{2}V\textstyle\sum_q \tilde{A}_q|\eta_q|^2, \tag{6}$$

where

$$\tilde{A}_q = \tilde{A} - \kappa q^2 + \lambda q^4. \tag{7}$$

The instability of the β phase with respect to the soft mode with the amplitude η_q occurs for the wave vector which minimizes $\tilde{A}_q$, i.e., for

$$q_0^2 = \kappa/2\lambda. \tag{8}$$

The transition temperatures T_{c1} and T_{c2} determining the boundaries of the incommensurate γ phase—i.e., the boundaries of the region where η_{q_0} has a nonzero static value—are obtained from $\tilde{A}_{q_0} = 0$ as

$$T_{c1,2} = T_0 + \frac{D^2}{2C^2F}\left[-\tilde{a} \pm \left(\tilde{a}^2 + \frac{4C^2F}{D^2}\,\lambda q_0^4\right)^{1/2}\right]. \tag{9}$$

Between T_{c1} and T_{c2} we have $\tilde{A}_{q_0} < 0$ and η_{q_0} is nonzero. It is obtained from a plane-wave solution of the nonlinear Euler equation

$$\lambda\, d^4\eta/dx^4 + \kappa\, d^2\eta/dx^2 + \tilde{A}\eta + \tilde{B}\eta^2\eta^* = 0 \tag{10}$$

as

$$\eta_{q_0}^2 = -(\tilde{A} - \lambda q_0^4)/\tilde{B}. \tag{11}$$

It should be noted that in the general case the solution of Eq. (10) can be expressed in terms of elliptic functions. For C3Mn, however, the solution seems to be adequately represented by a plane wave.

Above T_{c1} and below T_{c2} the static part of the

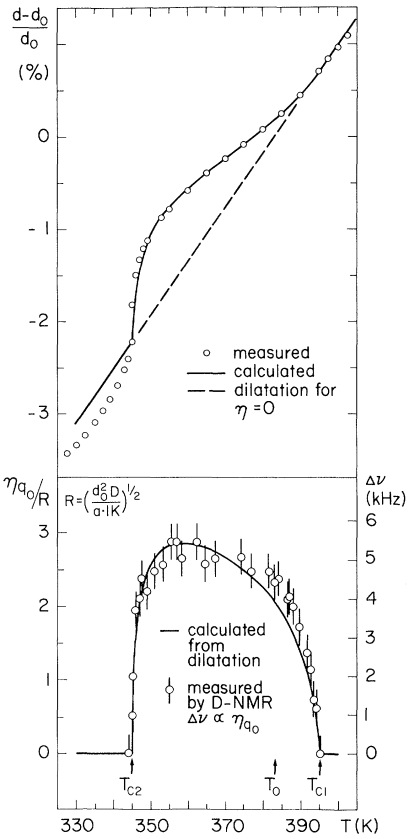

FIG. 3. Comparison between the predicted—Eqs. (3) and (11)—and observed temperature dependences of the modulation amplitude η_{q_0} and the interlayer distance d-d_0. The modulation amplitude $\eta_{q_0} \propto \Delta\nu$ has been measured by deuteron NMR (Refs. 6 and 7), whereas $(d-d_0)/d_0$ has been determined by thermal expansion measurements. The peak-to-peak modulation of the tilt angle of the propylammonium groups in the middle of the I phase amounts to 8 deg.

soft-mode amplitude vanishes, $\eta_{q_0}=0$, and we get a reentrant $\beta=\delta$ phase below T_{c2}. In contrast to incommensurate systems not exhibiting a reentrant behavior the modulation wave vector q_0 should be practically temperature independent throughout the whole I phase. In the range between T_{c1} and T_{c2} the temperature dependence of the interlayer distance should be anomalous too.

The amplitude of the incommensurate modulation of the tilt angle of the propylammonium groups, η_{q_0}, was observed[6] via a measurement of the temperature dependence of the splitting of the sharp edge singularities of the incommensurate frequency distribution[7] of the quadrupole-perturbed-ND_3 deuteron magnetic resonance spectra. The spatial modulation of the propylammonium tilt angle namely leads to a typical deuteron frequency distribution with sharp edge singularities[6,7] which correspond to the maximum modulation angle, i.e., to the amplitude of the order parameter. The maximum spitting in the middle of the I phase yields a peak-to-peak modulation of 8 deg. The vanishing of the amplitude at T_{c1} and T_{c2} is clearly observable (Fig. 3). The anomalous temperature dependence of the average interlayer distance was studied by measuring the thermal expansion of the crystal in a direction perpendicular to the layers. The experimental data are compared with the predictions of the Landau theory in Fig. 3 and the agreement seems to be rather good.

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[a]On leave from J. Stefan Institute, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia.

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