Anomalous Phase Transitions in LiCsSO₄ in the Compressible hcp Ising Model

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Structural low-temperature phase transformations in LiCsSO₄ are analysed in a newly tailored simple model of the static soliton in the periodically modulated phases of the one-dimensional compressible Ising model. It is shown that the original hcp symmetry is crucial for understanding of the anomalous temperature-dependence of the Brillouin shift.

PACS: 78.35.+c, 75.10.Hk, 62.20.D–

1. Introduction

The main objective of the paper is to derive a compressible hcp Ising model in which planar rotations of SO₄ tetrahedrons in LiCsSO₄ (LCS) are coupled to acoustic phonons [1]. The model provides a simple interpretation of empirically observed anomalous low-temperature variation of the frequency shift in inelastic Brillouin light scattering [2–4]. We focus our attention on the longitudinal phonon γ₁, travelling along one of the basic orthorhombic axes, b, because the result obtained for this direction is especially interesting (see Fig. 1).

![Graph of Brillouin shift vs. temperature](image)

Fig. 1. Results of the Brillouin light scattering for the longitudinal phonon γ₁, propagating along the [010] direction. The horizontal line crosses the curve at the temperatures where the Brillouin shift is equal to that at T₁.

The LCS crystal belongs to the family of the general formula A⁺A⁻BX₄. All the compounds of the family can be presented as a set of BX₄ tetrahedrons and A⁺⁺ cations which are placed in the sites of a hcp structure. The latter actually consists of two interpenetrating simple hexagonal Bravais lattices which fact appears to be crucial in our introduction of two order parameters. The A⁺⁺ cations form a regular simple hexagonal lattice.

It is generally accepted that a sequence of structural phase transitions in LCS is determined by a competition between two types of doubly degenerate orientations of the SO₄ tetrahedrons in the cationic environment: the first is the up/down orientation of the tetrahedron apexes, and the second one is associated with the clockwise vs. anticlockwise rotations of the tetrahedrons around the orthorhombic axis, c.

The up/down orientation is established at relatively high temperatures, for instance, at T = 600 K in LCS, and remains constant with decreasing temperature. It breaks the original hexagonal symmetry P6₃/mmc and drives the sequence of structural transformations when the temperature decreases. The structural transformations of the rotational ordering typically occur at much lower temperatures (near T = 200 K in LCS [2]).

The crystal undergoes a ferroelastic order–disorder phase transition from orthorhombic Pmca to monoclinic P112₁/n phase at T₁ = 201 K.

Within the framework of the two-spin hcp Ising model [5–8] both the up/down and rotational orientations can be described by two binary S = 1/2 spin variables with exchange interactions between the neighbouring tetrahedrons. Since, in the present paper, we are dealing only with the low-temperature structural phase transitions, the model has been effectively reduced to the one-spin hcp Ising Hamiltonian with competing interactions, and with one spin S = 1/2 describing the clockwise and/or anticlockwise rotations of the BX₄ tetrahedrons. Moreover, considering electrostatic nature of the interactions...
between the tetrahedrons, we assume signs of the exchange parameters to be determined by the parallel or antiparallel mutual orientation of the respective tetrahedrons' apexes (see Fig. 2).

The Ising Hamiltonian is extended by an introduction of interaction between the spins and the acoustic phonons in a form which enables renormalisation of the phonon energies by the spin order. We believe that an origin of the intriguing behaviour of the Brillouin light scattering in LCS lies in the hcp crystal structure itself.

2. The structural phase transitions in the one-dimensional Ising model

The original Hamiltonian of the pseudo-spin system is the hcp spin-1/2 Ising model. To attain maximal simplicity, while preserving the essential features of the problem, we project the three-dimensional model onto the basic orthorhombic axis, \( b \), corresponding to that of the longitudinal phonon propagation, and obtain the Hamiltonian in the form

\[
\hat{H}_s = -(1/2) \sum_{i,j} J_{ij} \hat{S}_i \hat{S}_j,
\]

where the position indexes run over two mutually inter-penetrating identical chains, whose origins are shifted by \( b/3 \) with respect to each other. Exchange interactions are limited to those between the intra-chain \( (J_1 \) and \( \tilde{J}_1 \) \) and inter-chain \( (J_2 \) and \( \tilde{J}_2 \) \) nearest neighbors. Because of the local correlations between the vertical and planar orientations of SO\(_4\) tetrahedrons \cite{1, 7}, we assume that the nn exchange interactions can be either ferromagnetic \( (J_1 \) and \( J_2 \) \) or antiferromagnetic \( (J_1, J_2 \) \) in accordance with mutual vertical orientation of their apexes (see Fig. 2).

\( S_i \) describes the thermal average of spin density per unit area perpendicular to the axis \( b \):

\[
S(y) = \int dx \, dz \, S(x, y, z),
\]

where \( S_i \) is substituted with an appropriate continuous function of \( y \). The order parameter \( S_{q_\theta}(y) \) describes a net spin density wave per unit area perpendicular to the axis \( b \). It is assumed in a simple form

\[
S_{q_\theta}(y) = B(T) \exp(iq_\theta(T)y).
\]

The amplitude \( B(T) \) is temperature dependent, while the phase is both temperature dependent and allowed to be space dependent in order to accommodate to the underlying lattice. The Fourier transform \( J(q_\theta) \) takes the form

\[
J(q_\theta) = J_1 + 2\tilde{J}_1 \cos \left( \frac{bq_\theta}{2} \right) + J_2 \cos \left( \frac{bq_\theta}{3} \right) + 2\tilde{J}_2 \cos \left( \frac{bq_\theta}{6} \right).
\]

The mean field order-disorder transition temperature \( T_c \) is given by the value for which the paramagnetic susceptibility first diverges as the temperature is lowered. The wave vector \( q_\theta \) at \( T_c \) is determined by equalisation to zero of the first derivative of \( J(q_\theta) \). The equation is quadratic and its both real roots fulfil the sufficient condition for the maximum of \( J(q_\theta) \):

\[
12\tilde{J}_1 \left[ \cos \left( \frac{bq_\theta}{6} \right) \right]^2 + 2J_2 \cos \left( \frac{bq_\theta}{6} \right) + \tilde{J}_2 - 3\tilde{J}_1 = 0.
\]

The crystal symmetry, reflected in that of the modelling chain, selects two equally valid wave vectors, corresponding to two phase transition temperatures. The higher of them is equal to \( T_1 \). Below \( T_1 \) the periodicity of the spin structure changes in a stepwise manner. For a maximum possible insight into the empirical data, it is important to study the simplest possible staircase consisting of two commensurate steps separated by an incommensurate phase. With decreasing temperature, the system undergoes first a commensurate-to-incommensurate phase transition (at \( T = T' \) and then, at \( T = T_2 \), a reversed lock-in phase transition to the collinear commensurate phase. Stability of the commensurate phases can be understood within the soliton-lattice picture. The solitons are domain walls which form a regular lattice with either commensurate or incommensurate translational symmetry described by the wave vector \( q_\theta \). In the commensurate phase, the standard minimisation of the free-energy expansion up to the fourth order with respect to the order parameter yields for the amplitude

\[
B^2(T)/3 = \frac{|J(q_\theta) - T|}{T},
\]

where \( q_\theta \) is the appropriate commensurate modulation vector. Temperatures at which the amplitude of the order parameter becomes equal to zero are indicated in Fig. 1 as those at which the Brillouin shift is the same as that at \( T = T_1 \). Actually those are not the incommensurate-to-commensurate phase transition temperatures \( T_{C_2} \), equal to \( T_2 \) and \( T' \), respectively (see Fig. 1). The latter, found from the soliton theory as those at which the system becomes unstable with respect to soliton formation, are equal to...
TCP = J(qx) + a^2/4c,  \tag{7}

where \( a = -\frac{1}{2} \sin \left( \frac{b y_1}{2} \right) - \frac{1}{2} \sin \left( \frac{b y_2}{2} \right) - \frac{1}{2} \sin \left( \frac{b y_3}{2} \right) \) and \( c = -\frac{1}{2} \cos \left( \frac{b x_1}{2} \right) - \frac{1}{2} \cos \left( \frac{b x_2}{2} \right) - \frac{1}{2} \cos \left( \frac{b x_3}{2} \right) \) are the respective linear and second-order coefficients of the power-series expansion of the Fourier transform \( J(qx) \) in terms of small deviations from the commensurate modulation vector, \( q\mathbf{x} \). \[ 0-12 \]. At TCP, the commensurate wave vector changes its length by the limiting value, equal to \(-a/2c\) [9]. Our notation is deliberately analogous to that used by Bak and Boehm in Ref. [9]. As seen from Eq. (7), it is the sign of \( c \) which determines a relation between two temperatures of the phase transition.

3. The compressible Ising model

Following the notion of Oitmaa [13], we expand the exchange integral \( J_{ij} \) in the Ising model up to the second order in the spin displacements. Introducing the phonon variables \( \{\tilde{a}_{k_{1}}, \tilde{a}_{k_{2}}, \tilde{a}_{k_{3}}\} \) we arrive, in the reciprocal lattice, at an effective spin-phonon coupling [14]:

\[ \tilde{H}_{\text{spin}} = \sum_{k_{1}, q_{0}} D(k_{1}, q_{0}) S_{q_{0}} \tilde{S}_{-q_{0}} \tilde{a}_{k_{1}} \tilde{a}_{k_{1}}, \tag{8} \]

where we have preserved only the terms, which can renormalise the phonon frequencies. The formula for the coupling parameter \( D(k_{1}, q_{0}) \) remains in good agreement with that obtained in [12, 13]. For more convenience, it is later substituted by a constant.

Since the Ising model has no dynamics of its own, the spin system can be recognised as static, while the lattice vibrations as fast variables. This recognition enables us to average the spin-phonon coupling over the states of the uncoupled Ising system which, in turn, yields an explicit expression for the renormalised phonon frequency

\[ \tilde{\omega}_{k_{1}} = \omega_{k_{1}} + \sum_{q_{0}} D(k_{1}, q_{0}) \langle S_{q_{0}} S_{-q_{0}} \rangle. \tag{9} \]

The spin correlation \( \langle S_{q_{0}} S_{-q_{0}} \rangle \) is calculated in the mean-field approximation as a product of two order parameters \( \langle S_{q_{0}} S_{-q_{0}} \rangle = S_{q_{0}} S_{-q_{0}} \). From Eq. (3), we obtain that

\[ \tilde{\omega}_{k_{1}} = \omega_{k_{1}} + D(k_{1}) B^{2}(T). \tag{10} \]

4. Conclusions

For the end of this paper, we briefly summarise the main conclusions.

1) We propose the original model of the ferroelastic low-temperature phase transitions in LiCsSO\(_{4}\) has been tailored for the needs of this specific system. The model melts together three components: the mean-field theory of the structural phase transitions in the A\(^{+}\)A\(^{-}\)BX\(_{4}\) family with the extended version of the Bak soliton theory of the commensurate-incommensurate phase transitions in the one-dimensional Ising model. The third component is the pseudo-spin–phonon interaction derived in the framework of the compressible Ising Hamiltonian.

2) We make an extensive use of the hcp symmetry of the system that allows us to introduce the complex order parameters.

3) We assume that below the order– disorder phase transition, the system undergoes the staircase consisting of three phases: the commensurate and incommensurate phases with modulation along the \( b \)-axis and, finally, the low-temperature lock-in collinear phase. It means that with increasing/decreasing temperature, the system undergoes commensurate-to-incommensurate and the reversed incommensurate-to-commensurate phase transitions. And, apart from them, the order–disorder one at \( T = T_{p} \). The succession of the phase transitions turns out to be crucial for interpretation of the empirical result of the Brillouin scattering.

4) The temperature at which the amplitude of the order parameter goes to zero is not identical with that of the commensurate-incommensurate phase transition. This difference plays an important role in calculation of the temperature-dependent renormalisation of the phonon frequency, caused by the phonon scattering on the spin structure.

5) We can find simple relations between the empirical temperatures of the anomalies found in the Brillouin scattering and the interaction parameters of the Ising model.

6) The spin-phonon interaction gives rise to dynamics, which, otherwise, is not present in the Ising model.

References