

Pressure-induced temperature shift of the lock-in transition in some A_2BX_4 crystals

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The influence of hydrostatic stress on phase transitions of a “Lifshitz type-I” system is discussed. Taking into account third- and fifth-order coupling terms between the order parameter and the strains, we show that the two lowest-order terms in the Landau free-energy expansion are both pressure dependent. Within the “phase-modulation-only” approximation, a formula is derived, which gives the shift of the lock-in transition temperature under the effect of a stress. A numerical comparison with the Clausius-Clapeyron relation is shown.

The subject of this paper is the influence of hydrostatic pressure on the successive phase transitions induced by the instability of an irreducible representation from which the Lifshitz invariant can be constructed. The normal-incommensurate transition is of the second order for a system satisfying this condition and the pressure-induced shift of the transition temperature is described by the Ehrenfest relation, in reasonable agreement with experimental results. On the other hand, the order of the lock-in phase transition is not clearly established. In the framework of the Landau theory of second-order phase transitions, we derive a formula giving, from the knowledge of the pressure-induced shift of the normal-incommensurate transition temperature, the displacement of the lock-in transition temperature under the effect of a hydrostatic stress. The numerical result, in the case of potassium selenate, of which several thermophysical quantities are available in the literature, is compared with those obtained from the Clausius-Clapeyron relation which is valid for a first-order phase transition. Although this study focuses on K_2SeO_4 , it can be extended to other compounds and, in particular, to its isomorphs.

Potassium selenate undergoes a second-order transition at $T_i \simeq 128$ K from the normal $Pnam$ phase to an incommensurate phase, with a modulated wave vector $q_0 = (1 - \delta)a^*/3$, and then a lock-in transition to the commensurate ferroelectric $Pna2_1$ phase with the unit cell tripled along the a axis. The relevant free-energy density can be written in terms of basis variables Q and Q^* belonging to the Σ_2 representation of the small group C_{2v} at $q_c = \frac{1}{3}a^*$, from which the Lifshitz invariant of the form

$$Q \left[\frac{\partial Q^*}{\partial x} \right] - Q^* \left[\frac{\partial Q}{\partial x} \right]$$

is constructed:

$$F = \int F(x) dx / \int dx ,$$

in which

$$F(x) = \frac{1}{2}a\eta^2 + \frac{1}{4}b\eta^4 + \frac{1}{4}c'\eta^6 + \frac{1}{4}c\eta^6 \cos 6\theta - d\eta^2 \left[\frac{\partial \theta}{\partial x} \right] + \frac{1}{2}f \left[\eta^2 \left[\frac{\partial \theta}{\partial x} \right]^2 + \left[\frac{\partial \eta}{\partial x} \right]^2 \right], \tag{1}$$

with $a = a_T(T - T_0)$ and $Q = (1/\sqrt{2})\eta e^{j\theta}$.

The coefficients a_T , b , c' , c , and f are assumed to be positive. Within the “phase-modulation-only” approximation, the equilibrium local phase variable is given by the multisoliton solution of the sine-Gordon equation

$$\theta_0(x) = \frac{1}{3} \text{am} \left[\frac{\nu}{\gamma} x, \gamma \right]$$

with $\nu = 3\eta^2 \sqrt{c/f}$. $\text{am}(u, \gamma)$ is a Jacobian elliptic function and γ is the modulus of the elliptic functions. The spatial variations of the phase variable satisfy the relation

$$3\theta_0(x + \lambda) = 3\theta_0(x) + \pi$$

in which $\lambda = 2\gamma K(\gamma)/\nu$ is the intersoliton distance fixed by the period of $\text{am}(u, \gamma)$. $K(\gamma)$ is the complete elliptic integral of the first kind. Inserting $\theta_0(x)$ into (1) and integrating over one period, one finds the ground-state energy per unit length:¹

$$F = \frac{1}{2}a\eta^2 + \frac{1}{4}\eta^4 \left[b - \frac{2\pi d}{\gamma K(\gamma)} \sqrt{c/f} \right] + \frac{1}{4}\eta^6 \left\{ c' + c \left[1 + \frac{4}{\gamma^2} \left(\frac{E(\gamma)}{K(\gamma)} - \frac{1}{2} \right) \right] \right\}, \tag{2}$$

where $E(\gamma)$ is the complete elliptic integral of the second kind. Minimizing (2) with respect to γ and η leads to the following system of equations:

$$\frac{2E(\gamma)}{\gamma} \eta^2 - \frac{\pi d}{\sqrt{fc}} = 0, \quad T \geq T_1, \tag{3a}$$

$$a + \eta^2 \left[b - \frac{2\pi d}{\gamma K(\gamma)} \sqrt{c/f} \right] + \frac{3}{2}\eta^4 \left\{ c' + c \left[1 + \frac{4}{\gamma^2} \left(\frac{E(\gamma)}{K(\gamma)} - \frac{1}{2} \right) \right] \right\} = 0. \tag{3b}$$

T_1 is the lock-in transition temperature. The coefficients involved in (3) can be estimated from experiment (see, for example, Refs. 2–4). The temperature dependence of both the modulus γ and the order-parameter η can be deduced from the above system by computation.⁵ Neither

saturation nor the discontinuity of η near T_1 , suggested previously in Refs. 6 and 7, has been found. It is probably due to the small value of the lock-in energy provided by the sixth-order term. The coefficient d will be assumed positive. The lock-in transition temperature is reached for $\gamma=1$:

$$T_1 = T_0 - \frac{\pi b d}{2 a_T \sqrt{f c}} - \frac{3(c' - c)\pi^2 d^2}{8 a_T f c}. \quad (4)$$

$T_0 = (T_i - d^2/a_T f)$ differs from the actual second-order temperature T_i by a small amount (~ 0.7 K), which can be neglected.^{2,4} In order to derive the shift of the lock-in transition temperature under the effect of the hydrostatic stress, we introduce in (1) the following terms:

$$\sum_k h_k e_k \eta^2 + \sum_k g_k e_k \eta^4 + \frac{1}{2} \sum_{k,k'} C_{kk'}^0 e_k e_{k'} + p \sum_k e_k, \quad (5)$$

$k, k' = 1, 2, 3$.

The first two terms are the third- and the fifth-order coupling terms between the strains e_k and the order parameter. This latter coupling is introduced in order to take into account the nonlinear temperature dependence of the measured strains.^{8,9} The next term is the elastic energy while p stands for the hydrostatic pressure. Replacing the strains by their spontaneous values,

$$e_k^s = - \sum_{k'} S_{kk'}^0 (h_{k'} + g_{k'} \eta^2) \eta^2 - p \sum_{k'} S_{kk'}^0, \quad (6)$$

leads to the renormalization of the coefficients a , b , and c' involved in the previous equations:

$$a(p) = a - 2p \sum_{k,k'} h_k S_{kk'}^0, \quad (7a)$$

$$b(p) = b' - 4p \sum_{k,k'} g_k S_{kk'}^0 \quad \text{with} \quad b' = b - 2 \sum_{k,k'} S_{kk'}^0 h_k h_{k'}, \quad (7b)$$

$$c'' = c' - 4 \sum_{k,k'} g_k h_{k'} S_{kk'}^0. \quad (7c)$$

A term of eighth order and a term of the form

$$\frac{p^2}{2} \sum_{k,k'} S_{kk'}^0,$$

which do not play any role here, have been dropped. The coefficients c and c' can also be considered renormalized by the fourth-order coupling terms, which do not appear explicitly in the text, between the order parameter and the shear strain e_5 on one hand and the polarization, lying along the c axis, on the other hand. $S_{kk'}^0$ is the elastic compliance tensor for $T \geq T_0$. Taking into account (7b), the differentiation of Eq. (4) with respect to pressure leads to

$$\frac{dT_1}{dp} = \frac{dT_0}{dp} + \left[\frac{2\pi d}{a_T \sqrt{f c}} \right] \sum_{k,k'} g_k S_{kk'}^0. \quad (8)$$

This formula, which is the main result of this paper, gives the shift of the lock-in transition temperature under the influence of a hydrostatic pressure. The first term on the

right-hand side gives the displacement of the second-order transition temperature while the second term, explicitly involving the Lifshitz contribution (d term), gives the rate of change of the temperature range for the stability of the incommensurate phase. Result (8) is valid for compounds showing a linear pressure shifting of the phase-transition temperatures. With use of Eq. (7a), the shift of the normal-incommensurate transition temperature can be written as

$$\frac{dT_0}{dp} = \frac{2}{a_T} \sum_{k,k'} h_k S_{kk'}^0. \quad (9)$$

Such a result can also be derived from the thermodynamic Ehrenfest relation,¹⁰

$$\frac{dT_0}{dp} = T_0 \frac{\Delta \alpha_v}{\Delta C_s}, \quad (10)$$

where

$$\Delta \alpha_v = \frac{a_T}{b'} \sum_{k,k'} h_{k'} S_{kk'}^0, \quad (11)$$

and

$$\Delta C_s = \frac{T_0 a_T^2}{2b'}. \quad (12)$$

represent, respectively, the discontinuities of the volume thermal expansion coefficient and of the specific heat at constant pressure. When the lock-in phase transition is clearly of the first order, the term on the left-hand side of Eq. (8) is given by the Clausius-Clapeyron relation,¹⁰

$$\frac{dT_1}{dp} = \frac{\Delta V}{\Delta S}, \quad (13)$$

in which ΔV and ΔS are the changes of the volume and of the entropy at the lock-in transition.

Let us now give a numerical application of formula (8) in the case of potassium selenate, which has been intensively investigated in the last decade. In order to estimate the second term on the right-hand side of Eq. (8), the temperature dependence of the spontaneous strains, measured at atmospheric pressure,⁸ have been fitted by expression (6) using the sums

$$\Delta \beta_k = \sum_{k'} S_{kk'}^0 g_{k'}$$

($k, k' = 1, 2, 3$) as free parameters. The temperature dependence of the square of the order-parameter amplitude has been approximated by the classical law $a_T(T_0 - T)/b'$. The value of $a_T = 1.5 \times 10^{23} \text{ s}^{-2} \text{ K}^{-1}$ can be deduced from the temperature dependence of the soft-mode frequency¹¹ at $q = q_0$, while the value of $b' = 1.1 \times 10^{42} \text{ dyn}^{-1} \text{ cm}^2 \text{ s}^{-4}$ can be deduced from Eq. (12). The excess value of the specific heat $\Delta C_s = 1.3 \times 10^6 \text{ dyn cm}^{-2} \text{ K}^{-1}$ at $T = T_i$ has been measured by the authors of Refs. 12 and 13. We used the following values of

$S_{kk}^0 = \{2.0, 2.4, 3.3\} \times 10^{-12} \text{ dyn}^{-1} \text{ cm}^2$ (see Ref. 14) and those of

$$S_{12,13,23}^0 = \{-0.6, -0.5, -1.3\} \times 10^{-12} \text{ dyn}^{-1} \text{ cm}^2$$

(see Refs. 2 and 3). The values of the coefficients

$$h_i = \{0.3, 0.5, -3.8\} \times 10^{26} \text{ s}^{-2}$$

can be deduced from the values of

$$\frac{dT_0}{d\sigma_i} = \{3.1, 7.7, -17.0\} \text{ K kbar}^{-1}$$

given in Ref. 15 or from the discontinuities of the thermal expansion coefficients¹³. σ_i is an uniaxial stress. The pressure-induced shift of the normal-incommensurate transition temperature estimated from Eq. (10) is in good agreement with the experimental results given in Refs. 16–18. The best fit of the main spontaneous strain along the c axis, which has been measured⁸ with a reasonable accuracy ($\sim 10\%$), is shown in Fig. 1. The fitted value of $\Delta\beta_3$ was found equal to $14.5 \times 10^{31} \text{ dyn}^{-2} \text{ cm}^4 \text{ s}^{-4}$. It shows that the effect of an uniaxial compressive stress along the c axis leads to an increase of the lock-in transition temperature (see below) while this latter decreases under the effect of a hydrostatic pressure.^{16,18} The contribution of both $\Delta\beta_1$ and $\Delta\beta_2$ should then produce this required decrease of the lock-in transition temperature. The values -5.5×10^{31} and $-10.5 \times 10^{31} \text{ dyn}^{-2} \text{ cm}^4 \text{ s}^{-4}$ for $\Delta\beta_1$ and $\Delta\beta_2$, respectively, could fit the temperature dependence of the spontaneous strains along the a and b axes, which have been measured with high inaccuracy (see Fig. 1). The values of $\Delta\beta_1$ and $\Delta\beta_2$ also match the pressure-induced shift of T_1 as will be shown in what follows.

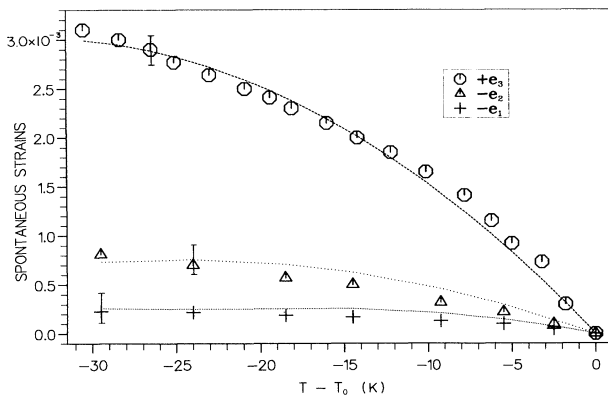


FIG. 1. Temperature dependence of the spontaneous strains (from Ref. 8). The upper curve is the best fit of e_3^s (open circles). The fitted value of $\Delta\beta_3$ was found to be equal to $14.5 \times 10^{31} \text{ dyn}^{-2} \text{ cm}^4 \text{ s}^{-4}$. The two lower curves have been obtained with $\Delta\beta_1$ equal to $-5.5 \times 10^{31} \text{ dyn}^{-2} \text{ cm}^4 \text{ s}^{-4}$ and $\Delta\beta_2$ equal to $-10.5 \times 10^{31} \text{ dyn}^{-2} \text{ cm}^4 \text{ s}^{-4}$. Note that e_1^s (crosses) and e_2^s (triangles) are negative.

The knowledge of the $\Delta\beta_k$ sums allows us to estimate the values of the coefficients

$$g_k = \{-3.3, -3.9, 2.3\} \times 10^{43} \text{ dyn}^{-1} \text{ cm}^2 \text{ s}^{-4}$$

and the value of the second term on the right-hand side of formula (8):

$$\left(\frac{2\pi d}{a_T \sqrt{fc}} \right) \sum_k \Delta\beta_k = -2.0 \text{ K kbar}^{-1}. \quad (14)$$

The coefficient $f = 2.5 \times 10^{10} \text{ cm}^2 \text{ s}^{-2}$, which is the curvature of the soft mode along a^* , can be known from neutron measurements.¹¹ The coefficient $d = f \Delta q$, with $\Delta q = |q_0 - q_c| = \frac{1}{3} \delta_0 a^*$ near T_0 , is equal to $5.0 \times 10^{16} \text{ cm s}^{-2}$. $\delta_0 = 0.07$ is the value of δ at $T \lesssim T_0$ and the lattice parameter along the a axis is equal to $7.6 \times 10^{-8} \text{ cm}$. The value of the coefficient $c = 1.0 \times 10^{58} \text{ dyn}^{-2} \text{ cm}^4 \text{ s}^{-6}$ can be deduced from Eq. (4) by fixing the value of $T_1 = 93 \text{ K}$ and neglecting the second part on the right-hand side which comes from the sixth-order terms. The value of coefficient c has been underestimated in Ref. 4. The displacement of the lock-in phase-transition temperature calculated by means of formula (8) is then

$$\frac{dT_1}{dp} = -8.5 \text{ K kbar}^{-1}. \quad (15)$$

An average value of $dT_0/dp = -6.5 \text{ K kbar}^{-1}$ has been considered.^{15–18} Taking into account the large uncertainties involved in the values of the various coefficients, one can consider this result to be in reasonable agreement with the experimental values -9.0 and $-11.4 \text{ K kbar}^{-1}$ given in Refs. 16 and 18, respectively.

Let us estimate the pressure-induced shift of the lock-in transition temperature from the Clausius-Clapeyron relation. Values of 2.4×10^{-3} , 5.0×10^{-3} , and $7.2 \times 10^{-3} \text{ cal mol}^{-1} \text{ K}^{-1}$ were obtained in Refs. 13, 12, and 19 for the discontinuity of the entropy at $T = T_1$. Changes of volume at $T = T_1$ equal to -1.5×10^{-5} and -3.6×10^{-5} were reported by the authors of Refs. 13 and 9, respectively, while the authors of Refs. 8 and 20 have not detected any change of volume. Considering only their own measurements, the authors of Ref. 13 have found that the shift of the lock-in transition temperature is about -13 K kbar^{-1} . A value of $-12.6 \text{ K kbar}^{-1}$ has been estimated by the author of Ref. 9 by using the value of ΔS obtained in Ref. 12 and his own measurement of ΔV .

The large experimental discrepancies mentioned above do not allow one to draw definite conclusions. To confirm the difference (or the similarity) between the result estimated from relation (8) derived here and the result estimated from the Clausius-Clapeyron relation, careful measurements of the main physical quantities involved in the problem are required.

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