# Thermodynamics of the incommensurate state in $Rb_2WO_4$:
## The Lifshitz point in $A_2BX_4$ compounds

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We consider the evolution of the phase transition from the parent hexagonal phase $P6_3/mmc$ to the orthorhombic phase $Pmcn$ that occurs in several compounds of the $A_2BX_4$ family and depends on the hcp lattice parameter $c/a$. For compounds of $K_2SO_4$ type with $c/a$ larger than the threshold value 1.26 the direct first-order transition $Pmcn \leftrightarrow P6_3/mmc$ is characterized by a large entropy jump $\sim R\ln 2$. For compounds $Rb_2WO_4, K_2MoO_4, K_2WO_4$ with $c/a < 1.26$ this transition occurs via an intermediate incommensurate (Inc) phase. Differential scanning calorimetry measurements were performed in $Rb_2WO_4$ to characterize the thermodynamics of the $Pmcn \leftrightarrow Inc \leftrightarrow P6_3/mmc$ transitions. It was found that both transitions are again of the first order with entropy jumps $0.2 \cdot R\ln 2$ and $0.3 \cdot R\ln 2$. Therefore at $c/a \sim 1.26$ the $A_2BX_4$ compounds reveal an unusual Lifshitz point where three first-order transition lines meet. We propose the coupling of crystal elasticity with $BX_4$ tetrahedra orientation as a possible source of the transitions discontinuity.

## I. INTRODUCTION

The orientational ordering of $BX_4$ tetrahedra drives a rich sequence of structural phases in ionic $A_2BX_4$ compounds of $K_2SO_4$ type. In the present paper we are interested in the nature of the phase transition from the parent high-symmetry phase $P6_3/mmc$ ($\alpha$-$K_2SO_4$ type) to the orthorhombic phase $Pmcn$ ($\beta$-$K_2SO_4$ type) that occurs at high temperatures ($T \sim 600$–$800$ K) either directly,

$$Pmcn \overset{T_c}{\leftrightarrow} P6_3/mmc \qquad (1)$$

(e.g., in $K_2SO_4, Rb_2SeO_4, K_2SeO_4$), or via an intermediate $1q$-incommensurate (Inc) phase,

$$Pmcn \overset{T_l}{\leftrightarrow} Inc \overset{T_i}{\leftrightarrow} P6_3/mmc \qquad (2)$$
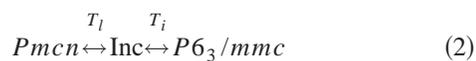
as in molybdates and tungstates $Rb_2WO_4$, $K_2MoO_4$, $K_2WO_4$. The last one has the modulation vector $\mathbf{q} = (0, q_b, 0)$ that can be alternatively directed in two other equivalent directions of the 120° star of the hexagonal Brillouin zone. All the transitions are of the order-disorder type and are characterized by the vertical (up/down) orientations of $BX_4$ tetrahedra with respect to the sixfold axis. Other low-temperature transitions in $A_2BX_4$ compounds that are related with the planar orientation of tetrahedra are beyond our consideration (for details, see Refs. 1–3).

From the viewpoint of the Landau theory of phase transitions, only the lock-in $Pmcn \leftrightarrow Inc$ transition should be of the first order. The $Pmcn \leftrightarrow P6_3/mmc$ transition should be of the second order since $Pmcn$ is a subgroup of $P6_3/mmc$

and in the Landau functional neither third-order nor Lifshitz terms are present. The transition $Inc \leftrightarrow P6_3/mmc$ should also be of the second order as a transition to the incommensurate phase of the type II. The recently proposed hcp Ising model[3] correctly describes the high-temperature phase diagram of $A_2BX_4$ compounds. In this model the $Pmcn \leftrightarrow P6_3/mmc$ and $Inc \leftrightarrow P6_3/mmc$ transitions are of the second order.

The experimental properties of the $Pmcn \leftrightarrow P6_3/mmc$ transitions in various compounds of $A_2BX_4$ family are collected from Refs. 4–10 in Table I as a function of the geometrical factor $c/a$ of their hcp structure. As was shown in our previous study[3] this is the unique parameter that drives the actual phase sequence: for $c/a > 1.26$ the transition is direct, whereas for $c/a < 1.26$ the sequence (2) takes place.

Contrary to the theoretical prediction based on the Landau and Lifshitz criteria, the direct $Pmcn \leftrightarrow P6_3/mmc$ transition is of the first order with a large jump of the molar entropy ($\sim R\ln 2$) (Refs. 7 and 9) and of the lattice constants ($\sim 2\%$).[5,6] The incommensurate phase in $Rb_2WO_4$, $K_2MoO_4$, $K_2WO_4$ was relatively poorly studied because they are highly hygroscopic.[10,11] It is known that the $Inc \leftrightarrow P6_3/mmc$ transition reveals a substantial discontinuity of the lattice parameter ($\sim 0.2$–$0.7\%$).[10] To characterize the thermodynamics of the $Pmcn \leftrightarrow Inc \leftrightarrow P6_3/mmc$ transition we performed differential scanning calorimetry (DSC) measurements in $Rb_2WO_4$ that are reported in Sec. II. It was found that both transitions are of the first order with entropy discontinuities of $0.2R\ln 2$ and $0.3R\ln 2$. The $Inc \leftrightarrow P6_3/mmc$ transition is a rare example of incommensurate transition that occurs discontinuously.

TABLE I. The critical temperatures $T_l$, $T_i$ for $Pmcn \leftrightarrow \text{Inc} \leftrightarrow P6_3/mmc$ transitions and $T_c$, for $Pmcn \leftrightarrow P6_3/mmc$ transitions, the molar entropy jumps and the lattice parameter jumps as functions of lattice parameter $c/a$. The entropy jumps in $Rb_2WO_4$ were measured in the present study.

| | $c/a$ | $T_l$,K | $T_i$,K $T_c$,K | $(\Delta S/R \ln 2)_{T_l}$ | $(\Delta S/R \ln 2)_{T_i}$ $(\Delta S/R \ln 2)_{T_c}$ | $(\Delta c/c)_{T_l}$ | $(\Delta c/c)_{T_i}$ $(\Delta c/c)_{T_c}$ |
|---|---|---|---|---|---|---|---|
| $K_2WO_4$ | 1.24 | 643 | 707 | | | <0.2% | 0.2% |
| $K_2MoO_4$ | 1.24 | 593 | 733 | | | <0.2% | 0.7% |
| $Rb_2WO_4$ | 1.25 | 660 | 746 | 0.2 | 0.3 | | |
| $Tl_2SeO_4$ | 1.26 | | 660 | | | | |
| $K_2SeO_4$ | 1.27 | | 745 | | 1.3 | | |
| $Rb_2MoO_4$ | 1.27 | | 775 | | | | |
| $Rb_2SeO_4$ | 1.29 | | 825 | | | | |
| $Cs_2SeO_4$ | 1.29 | | 860 | | | | |
| $K_2SO_4$ | 1.29 | | 860 | | 2.1 | | 2.5% |
| $Tl_2SO_4$ | 1.30 | | 773 | | | | <1.3% |

At $c/a \sim 1.26$ the critical temperatures $T_l, T_i, T_c$ coincide and the $A_2BX_4$ compounds seem to reveal a Lifshitz point which is defined as a triple point separating the high-temperature disordered phase and the low-temperature commensurate and incommensurate phases. The particular property of this point in $A_2BX_4$ compounds is that all incoming transition lines are of the first order. This possibility was theoretically studied in Ref. 12 where the discontinuities were modeled by the negative fourth-order terms in the Landau functional. Although in the conventional definition of the Lifshitz point (see, e.g., Refs. 13 and 14) the transitions to the low-temperature phases are considered to be continuous, we keep this notation since the origin of the triple point in $A_2BX_4$ compounds, considered in the present paper, is similar. Note that the realization of the Lifshitz point was found previously only in few experimental systems (for a review see Ref. 13). This is also an example of Lifshitz point in a system where the modulation vector can be oriented in more than one equivalent direction.

The main question raised by these systems is why strong discontinuities at $Pmcn \leftrightarrow P6_3/mmc$ and $\text{Inc} \leftrightarrow P6_3/mmc$ transitions appear. Note first that they cannot be ascribed to fluctuation effects that were widely studied during the last decades in relation with transitions to the modulated phases.[14–18] In such case the first-order character is attributed to the lack of a stable fixed point as in BaMnF$_4$ (Ref. 19) and the discontinuity is expected to be small due to the smallness of the critical region. We propose that the observed discontinuities are caused by the coupling of the order parameter with elasticity of the crystal that is known[20–22] to be able to change the order of transition. Introducing in Sec. III the corresponding coupling to the mean-field treatment of the hcp Ising model[3] and comparing the results with the measured jumps of the lattice constant and molar entropy, we demonstrate that this coupling can be responsible for the discontinuity of transitions.

## II. EXPERIMENT

DSC experiments were performed with $Rb_2WO_4$ crystals to characterize the thermodynamics of the $Pmcn \leftrightarrow \text{Inc} \leftrightarrow P6_3/mmc$ transitions. Due to the very high hygroscopic nature of the material, powder samples were prepared in a glove box in a dry nitrogen atmosphere. DSC experiments were performed using a Mettler-TA3000 equipment, between room temperature and 820 K. Recall that with this technique the DSC signal is a heat flow $dQ/dt$ that is equal to $mC_p dT/dt$, where $m$ is the mass of the sample. We optimize a temperature rate both on cooling and on heating at 5 K/min that allowed observation of the anomalies at the transitions. For larger rates the anomalies were smeared out because of the increasing temperature gradient.

In the region of a first-order phase transition, where both phases coexist, the DSC signal no longer obeys the equality $dQ/dt = mC_p dT/dt$. A latent heat is obtained by integration of the peak of the DSC signal over the coexistence region. The transition temperature is determined by the onset of the DSC peak.

The DSC thermograms of the investigated sample show the presence of two reversible enthalpy anomalies at about $T_l = 660$ K and $T_i = 746$ K, corresponding respectively to the lock-in and the incommensurate phase transitions (see Fig. 1). The measured molar entropy discontinuities are $\Delta S_{Tl} = 1.1$ J/K mol and $\Delta S_{Ti} = 1.8$ J/K mol. To determine the value of the entropy discontinuities at $T_i$, we integrated
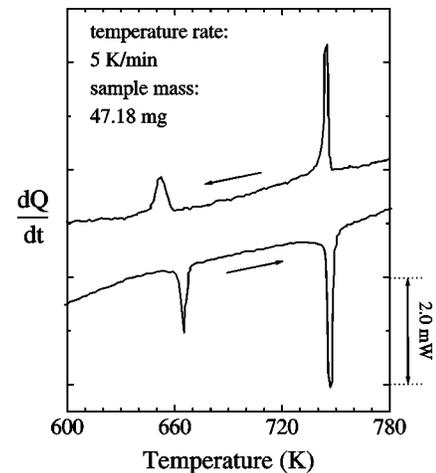


FIG. 1. DSC thermograms of $Rb_2WO_4$ in the region of $Pmcn \overset{T_l}{\leftrightarrow} \text{Inc} \overset{T_i}{\leftrightarrow} P6_3/mmc$ phase transitions on cooling and on heating.

the peak from about 8 K below $T_i$ since the DSC signal still varies in this temperature interval, see Fig. 1. The zone outside the sharp peak itself contributes for about 20% to $\Delta S_{Ti}$. These values are given in Table I in units of $R \ln 2$. A hysteresis of $6 \pm 2$ K was observed for the $Pmcn \leftrightarrow$ Inc transition, ($T_l = 662 \pm 1$ K for heating and $656 \pm 1$ K for cooling). In contrast, the Inc $\leftrightarrow P6_3/mmc$ transition, determined by the onset of the DSC peak, reveals no hysteresis within the error bar of $\pm 1$ K. This is consistent with the extremely small hysteresis of 1 K observed for $Pmcn \leftrightarrow P6_3/mmc$ transition in $K_2SO_4$.[8]

### III. DISCUSSION

The high-temperature order-disorder transitions in $A_2BX_4$ compounds are described by the in-site averages of the vertical orientation of $BX_4$ tetrahedra, $\sigma_i = \langle S_i \rangle$ where the pseudospin $S_i$ is equal to $\pm 1$ for the up/down tetrahedra orientations.[3] The variables $\sigma_i$ are equal to zero in the disordered high-temperature phase $P6_3/mmc$. In the low-temperature phase $Pmcn$, they take the equal amplitudes $\sigma_i = \pm \sigma$ and alternate according to $Pmcn$ symmetry. In the incommensurate phase a modulation $\sigma_i = \sigma_q(e^{i\mathbf{qr}_i} + e^{-i\mathbf{qr}_i}) = 2\sigma_q \cos \mathbf{qr}_i$ occurs. The absolute values of $\sigma_i$, and hence of amplitudes $\sigma$ and $2\sigma_q$ (that define the corresponding order parameters), are smaller than one; the smaller they are, the more $BX_4$ tetrahedra are disordered. Because of the discontinuity of the $Pmcn \leftrightarrow P6_3/mmc$ and Inc $\leftrightarrow P6_3/mmc$ transitions the amplitudes $\sigma$ and $2\sigma_q$ have nonvanishing values below the critical temperatures $T_c$ and $T_i$. We estimate $\sigma$ and $2\sigma_q$ in the ordered states from the entropy jump at the transition,

$$\frac{\Delta S}{R} = \left\langle \frac{1}{2}[(1+\sigma_i)\ln(1+\sigma_i) + (1-\sigma_i)\ln(1-\sigma_i)] \right\rangle_i,$$

(3)

that is measured experimentally (see Table I). For $K_2SeO_4$ and $K_2SO_4$, the inequality $\Delta S > R \ln 2$ holds, which means that in the low-temperature phase the $BX_4$ tetrahedra are perfectly ordered ($\sigma \sim 1$) and, possibly, other degrees of freedom are involved in the transition. Taking $\sigma_i$ in the incommensurate phase of $Rb_2WO_4$ as $2\sigma_q \cos \mathbf{qr}_i$, from $\Delta S = 0.3R \ln 2$, we get $2\sigma_q \sim 0.8$ that again demonstrates the high degree of tetrahedra ordering.

In the mean-field approach of the hcp Ising model,[3] the phase transitions from $P6_3/mmc$ to $Pmcn$ and to Inc phases were found to be continuous and the molecular free energy was expanded over the small values of parameters $\sigma$ and $2\sigma_q$ as

$$f_{com} = \frac{k}{2}(T - T_c)\sigma^2 + \frac{kT}{12}\sigma^4$$

(4)

for $Pmcn \leftrightarrow P6_3/mmc$ transition, and as

$$f_{inc} = \frac{k}{4}(T - T_i)(2\sigma_q)^2 + \frac{kT}{32}(2\sigma_q)^4$$

(5)

for Inc $\leftrightarrow P6_3/mmc$ transition.

The critical temperatures $T_c, T_i$ are functions of the interaction parameters $J_{ij}$. They coincide at the Lifshitz point

and are correlated with the geometrical factor $c/a$ as follows: $T_c < T_i$ when $c/a < 1.26$ and $T_c > T_i$ when $c/a > 1.26$.

To account for the discontinuity of the transitions we propose that the coupling of the tetrahedra orientation with crystal elasticity is responsible for this phenomenon. Our further consideration is analogous to the compressible Ising model, proposed by Domb.[20] To perform estimations we consider here only the coupling with the strain $e_3 = \Delta c/c$ along the sixfold axis and omit other elastic degrees of freedom. Taking into account these degrees of freedom is indeed difficult because of the absence of experimental data, but it would only improve our estimations.

The elastic contribution to the free energy is written as

$$f_{el} = \gamma\sigma^2 e_3 + \frac{1}{2}V_{mol}C_{33}e_3^2,$$

(6)

where $\gamma\sigma^2 e_3$ is the coupling of the order parameter with the elastic strain and $V_{mol}C_{33}e_3^2$ is the proper elastic energy of the crystal (per unit volume $V_{mol}$ of the molecule). Minimizing the elastic energy (6) with respect to $e_3$ we get the strain in the $Pmcn$ phase: $e_3 = -\gamma\sigma^2/V_{mol}C_{33}$. Substituting it back to Eq. (6) and taking into account Eq. (4) we find that the total free energy $f_{com} + f_{el}$ is written as

$$f_{com} + f_{el} = \frac{k}{2}(T - T_c)\sigma^2 + (kT/12 - \gamma^2/2C_{33}V_{mol})\sigma^4.$$

(7)

Therefore the coupling with the elastic strain renormalizes the quartic term $\sigma^4$ that becomes negative when the elastic contribution $\gamma^2/2C_{33}V_{mol}$ exceeds the Ising thermal energy $kT/12$. The transition is then of the first-order and the amplitude of the $Pmcn$ order parameter is stabilized by the higher-order terms.

We estimate the value of the coupling constant $\gamma$ from the relation $\gamma = -\Delta c/c \cdot V_{mol}C_{33}/\sigma^2$ that, in $K_2SO_4$ with $C_{33} = 55 \times 10^9$ N/m²,[23] $\sigma^2 \sim 1, V_{mol} \sim 120$ Å³$(1.2 \times 10^{-28}$ m³),[5] and $\Delta c/c = 0.025$, gives $\gamma \sim -1.7 \times 10^{-19}$ J. Then, the elastic contribution $\gamma^2/2C_{33}V_{mol} \sim 2.1 \times 10^{-21}$ J is larger than $kT_c/12 = 10^{-21}$ J, which justifies the role of the elastic degrees of freedom in the discontinuity of the $Pmcn \leftrightarrow P6_3/mmc$ transition.

Consider now the Inc $\leftrightarrow P6_3/mmc$ transition. Assuming that the elastic coupling is given by $\gamma\langle\sigma_i^2\rangle e_3 = \frac{1}{2}\gamma(2\sigma_q)^2 e_3$, we come to the effective functional

$$f_{inc} + f_{el} = \frac{k}{4}(T - T_i)(2\sigma_q)^2$$

$$+ (kT/32 - \gamma^2/8C_{33}V_{mol})(2\sigma_q)^4.$$

(8)

We perform the estimation of the quartic coefficient for $Rb_2WO_4$ in a way analogous to the previous, taking $2\sigma_q \sim 0.8$ and $V_{mol} \sim 142$ Å³$(1.42 \times 10^{-28}$ m³).[10] Since the elastic constant $C_{33}$ is not available we assume it has the same value as in $K_2SO_4$. The jump of the lattice parameter $\Delta c/c$ is assumed to be of the same order (namely 0.007) as in $K_2MoO_4$. The calculation gives: $\gamma = -2\Delta c/c \cdot V_{mol}C_{33}/(2\sigma_q)^2 \sim -2 \times 10^{-19}$ J and $\gamma^2/8C_{33}V_{mol} \sim 13 \times 10^{-22}$ J that again is larger than the bare fourth-order coefficient $kT_i/32 = 3 \times 10^{-22}$ J.

To conclude, we suggest that a Lifshitz point occurs in $A_2BX_4$ compounds at $c/a \sim 1.26$ where three first-order transition lines join. One can expect to reach this point experimentally, either in the $(x,T)$ phase diagram by preparing the solid solution $Rb_2W_xMo_{1-x}O_4$ or by subjecting $K_2SeO_4$ or $Tl_2SeO_4$ (with $c/a = 1.27$ and $1.26$) to a uniaxial pressure along $c$. Analyzing experimental data we demonstrated that the coupling of the order parameter with crystal elasticity is responsible for the discontinuity of the transition.

We stress another peculiar feature of the $Pmcn \leftrightarrow P6_3/mmc$ and $Inc \leftrightarrow P6_3/mmc$ transitions. Despite the strong entropy jump ($\sim R\ln 2$), they have very low hysteresis (less than 1 K) that cannot be explained on the basis of the available models.[20,21]

It is interesting to note that the $Pmcn \leftrightarrow P6_3/mmc$ transition occurs also in another related compound, $KLiSO_4$, that has a large ratio $c/a = 1.69$. Unlike other cases, this transition is either of the second or of the weak first order with the entropy jump less than $0.1 \cdot R\ln 2$ (Ref. 24) and with no detectable discontinuity of the lattice constants.[25] Then, it is quite probable that when $c/a$ increases, the transition becomes of the second order, and a tricritical point occurs on the $Pmcn \leftrightarrow P6_3/mmc$ transition line. More systematic experiments, however, are needed to verify this hypothesis.

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