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Stress-induced change of the Lifshitz point type in A_2BX_4 compounds

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Abstract

The high-temperature transition $P6_3/mmc$–$Pmcn$ in A_2BX_4 compounds is driven by the unique geometrical factor c/a of the hcp structure and occurs either directly for compounds with $c/a > 1.26$ or via an intermediate incommensurate phase for compounds with $c/a < 1.26$. We show that the prominent feature of the Lifshitz point that occurs at $c/a = 1.26$ is that all three incoming transition lines are of first order. We attribute this property to the interaction of the order parameter with the elastic degrees of freedom and classify the types of Lifshitz point that are possible in this case. We discuss the experimental properties of the Lifshitz point in A_2BX_4 compounds.

1. Introduction

A large number of structural transitions with the formation of an intermediate incommensurate ('Inc') phase that exists in between the low-temperature (LT) low-symmetry and high-temperature (HT) high-symmetry phases are known today. The systems revealing the so-called Lifshitz point in which the direct LT–HT transition transforms to the sequence LT–Inc–HT are of special interest [1–3]. Despite the numerous theoretical studies of the critical properties of the Lifshitz point, there are only a few experimental examples of such systems.

In the present paper we report on a special point that occurs in compounds of the A_2BX_4 family (of K_2SO_4 type) at HTs ($T \sim 600$–800 K) and we study its properties.

We propose to call this point a Lifshitz point and to generalize the definition of the Lifshitz point as given in [1–3] to the cases where first-order lines are found.

In the A_2BX_4 compounds the transition from the parent HT phase $P6_3/mmc$ to the LT orthorhombic phase $Pmcn$ can occur either directly:

$$Pmcn\text{–}P6_3/mmc \qquad (1)$$

as in K_2SO_4, Rb_2SeO_4, and K_2SeO_4 compounds or via an intermediate $1q$-incommensurate Inc phase:

$$Pmcn\text{–Inc–}P6_3/mmc \tag{2}$$

as in Rb_2WO_4, K_2MoO_4, and K_2WO_4 compounds [4, 5].

The theoretical aspects of the HT transitions in compounds of the A_2BX_4 family were studied in [6]. It was shown that the phase diagram of these compounds can be explained on the basis of Ising-like interaction between the vertical orientations of BX_4 tetrahedra located in the hexagonal close-packed structure. The inherent frustration of the hcp Ising model provides the observed transition sequence and explains the formation of the Inc phase. It is the unique parameter c/a of the hcp lattice that drives the transition sequence. When c/a is larger than the critical value 1.26 the direct transition (1) takes place, whereas when $c/a < 1.26$ the transition occurs first to an Inc phase. Therefore the threshold lattice parameter ratio $c/a = 1.26$ corresponds to a Lifshitz point on the T–c/a phase diagram.

In section 2 we review the experimental properties of A_2BX_4 compounds close to a Lifshitz point, including our DSC measurements for the Inc state in Rb_2WO_4 crystals. From these thermodynamic results it appears that the Lifshitz point in A_2BX_4 compounds is a point of special type, since all three incoming lines of LT–Inc, Inc–HT, and LT–HT transitions are of first order. In section 3 we discuss the Landau theory of HT transitions in A_2BX_4 compounds and attribute this peculiar property to the coupling of the vertical orientations of BX_4 tetrahedra with the elastic degrees of freedom. We study the general situation when the order parameter of the Inc phase is coupled with the crystal elasticity and show that three types of Lifshitz point are possible. Finally, we discuss the possibilities for further experimental studies of Lifshitz points in A_2BX_4 compounds.

Note that the Inc–HT and LT–HT transitions were supposed to be continuous in the original definition of a Lifshitz point. We generalize this definition to an arbitrary order of Inc–HT and LT–HT transitions and classify the different types of Lifshitz point according to the order of the incoming transition lines.

2. Thermodynamics of the Inc phase in A_2BX_4 compounds

The experimental properties of different compounds of the A_2BX_4 family are collected from [7–13] and presented in table 1 as a function of the lattice parameter c/a. The calorimetric properties of the $Pmcn$–Inc and Inc–$P6_3/mmc$ transitions are taken from our DSC measurements published in [5].

As follows from the data given in table 1, a Lifshitz point is indeed observed in A_2BX_4 compounds at $c/a \sim 1.26$.

We stress several important features of HT phase transitions in A_2BX_4 compounds (a more detailed analysis is given in [5]).

Note first that these first-order transitions are of the order–disorder type and are characterized by a large entropy jump close to $R\ln 2$ per BX_4 tetrahedron, which means that the BX_4 tetrahedra are practically frozen below the transition temperature.

Another important point is that all these transitions are characterized by a strong elastic discontinuity. The typical value of the lattice parameter jump along the c-axis is of 0.2–0.7% for the Inc–$P6_3/mmc$ transition and of 1–2.5% for the $Pmcn$–$P6_3/mmc$ transition. Despite these strong discontinuities, the hysteretic phenomena are small and do not exceed 1–2 K. It is noteworthy that the A_2BX_4 crystals are a rare example of compounds in which the Inc–HT transition occurs discontinuously.

Table 1. The critical temperatures T_l, T_i for $Pmcn$–Inc–$P6_3/mmc$ transitions and T_c for the $Pmcn$–$P6_3/mmc$ transition, and the corresponding jumps of the molar entropy.

	c/a	T_l (K)	T_c (K)	T_i (K)	$(\Delta S/R\ln 2)_{T_l}$	$(\Delta S/R\ln 2)_{T_c}$	$(\Delta S/R\ln 2)_{T_i}$
K_2WO_4	1.24	643		707			
K_2MO_4	1.24	593		733			
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_2Mo_4	1.27		775				
Rb_2SeO_4	1.29		825				
Cs_2SeO_4	1.29		860				
K_2SO_4	1.29		860			2.1	
Tl_2SO_4	1.30		773				

We discuss the role of the elastic degrees of freedom in HT transitions of A_2BX_4 compounds in the next section.

3. Theory of the stress-induced changes of Lifshitz point type

Consider now the theoretical aspects of HT transitions in A_2BX_4 compounds that are described by a single-component order parameter η [3]. From the viewpoint of Landau phase transition theory, only the lock-in transition $Pmcn$–Inc should be of first order. The $Pmcn$–$P6_3/mmc$ transition should be of second order since $Pmcn$ is a subgroup of $P6_3/mmc$ and neither third-order nor Lifshitz invariants can be constructed. The $P6_3/mmc$–Inc transition should also be of second order as a transition to an incommensurate phase of the type II. We attribute the discontinuities of these transitions to the interaction with the elastic degrees of freedom, that are known to be responsible for the change of phase transition order for structural transitions in crystals.

The corresponding Landau functional that describes both the Inc phase formation and the interaction of the order parameter with the elastic stress u is written as follows:

$$F = \tfrac{1}{2}a(T - T_c)\eta^2 + \tfrac{1}{4}b\eta^4 + \tfrac{1}{6}f\eta^6 + K(\nabla\eta)^2 + L(\nabla^2\eta)^2 + \tfrac{1}{2}Cu^2 + \gamma\eta^2 u \quad (3)$$

where the first three terms with $a, b, f > 0$ correspond to the standard Landau–Ginzburg–Devonshire free energy expansion, the term $\gamma\eta^2 u$ provides the coupling of the order parameter with the elastic stress, and the term $\frac{1}{2}Cu^2$ gives the elastic energy of the crystal.

Depending on the sign of the coefficient K, the transition from the $P6_3/mmc$ phase can occur either to the uniform phase $Pmcn$ or to the Inc phase.

(i) Assume $K > 0$

The direct transition to the $Pmcn$ phase with the uniform order parameter η_0 occurs. The minimization of (3) over u gives the stress of the crystal: $u = -(\gamma/C)\eta^2$. Substituting it back into (3), one obtains the effective Landau functional with removed elastic degrees of freedom:

$$F = \tfrac{1}{2}a(T - T_c)\eta_0^2 + \tfrac{1}{2}b(\tfrac{1}{2} - \kappa)\eta_0^4 + \tfrac{1}{6}f\eta_0^6 \quad (4)$$

where $\kappa = \gamma^2/Cb$ is the dimensionless coupling constant. It follows that the coupling with the elastic degrees of freedom renormalizes the fourth-order term. When the coupling is weak

($\kappa < \frac{1}{2}$), the second-order transition occurs at $T = T_c$. When the coupling constant is large ($\kappa > \frac{1}{2}$), the fourth-order term is negative and the first-order transition occurs at

$$T_c^* = T_c + \tfrac{3}{4} b^2 (\tfrac{1}{2} - \kappa)^2 / af. \tag{5}$$

(ii) Assume $K < 0$

The uniform order parameter is unstable with respect to the formation of a modulated phase and the $P6_3/mmc$–$Pmcn$ transition can occur via the intermediate Inc phase. To examine this possibility we substitute the modulated order parameter $\eta = \eta_q \cos qr$ into the functional (3) and average over the modulation period $2\pi/q$. Minimizing the functional over q and u we obtain that the transition occurs to the Inc phase with the modulation vector $q^2 = -K/2L$. The deformation of the crystal is estimated as $u = -(\gamma/2C)\eta_q^2$. Excluding the variables q and u we get the effective functional

$$F = \tfrac{1}{4} a (T - T_i) \eta_q^2 + \tfrac{1}{8} b (\tfrac{3}{4} - \kappa) \eta_q^4 + \tfrac{5}{96} f \eta_q^6, \tag{6}$$

where

$$T_i = T_c + \tfrac{1}{2} K^2 / aL. \tag{7}$$

Like in case (i), the Inc–$P6_3/mmc$ transition can be either of the second or the first order, depending on the sign of the fourth-order term that is provided by the strength of the elastic coupling constant κ. At $\kappa < \frac{3}{4}$ the transition occurs continuously at $T = T_i$, whereas at $\kappa > \frac{3}{4}$ the discontinuous transition takes place at

$$T_i^* = T_i + \tfrac{3}{10} b^2 (\tfrac{3}{4} - \kappa)^2 / af = T_c + \tfrac{1}{2} K^2 / aL + \tfrac{3}{10} b^2 (\tfrac{3}{4} - \kappa)^2 / af. \tag{8}$$

Summarizing now the calculations presented above, we can classify the elastically modified Lifshitz points as follows:

(a) The non-modified Lifshitz point of the $\mathrm{II_c II_i I_l}$ type (the Roman numeral means the order of transition whereas the subscript index indicates the type of transition: 'c' for the LT–HT transition, 'i' for the Inc–HT transition, and 'l' for the LT–Inc lock-in transition). This type of Lifshitz point occurs in the case of minimal elastic coupling when $\kappa < \frac{1}{2}$. The location of the $\mathrm{II_c II_i I_l}$ Lifshitz point is found from the equation $T_c = T_i$:

$$T_L = T_c, \qquad K_L = 0. \tag{9}$$

(b) The Lifshitz point of the $\mathrm{I_c II_i I_l}$ type that occurs in the case of moderate elastic coupling when $\frac{3}{4} > \kappa > \frac{1}{2}$. The location of the $\mathrm{I_c II_i I_l}$ Lifshitz point is found from the equation $T_c^* = T_i$:

$$T_L = T_c^*, \qquad K_L = (3L/2f)^{1/2} (\tfrac{1}{2} - \kappa) b. \tag{10}$$

(c) The Lifshitz point of the $\mathrm{I_c I_i I_l}$ type that occurs in the case of strong elastic coupling when $\kappa > \frac{3}{4}$. The location of the $\mathrm{I_c I_i I_l}$ Lifshitz point is found from the equation $T_c^* = T_i^*$:

$$T_L = T_c^*, \qquad K_L = -\left[\tfrac{3}{2} L b^2 (\tfrac{1}{2} - \kappa)^2 / f - \tfrac{3}{5} L b^2 (\tfrac{3}{4} - \kappa)^2 / f\right]^{1/2}. \tag{11}$$

As follows from our numerical estimations [5], the HT Lifshitz point in $\mathrm{A_2BX_4}$ compounds corresponds to this case.

In the vicinity of the Lifshitz point the modulation vector of the Inc phase is given by: $q^2 = -K_L/2L$. It tends to zero for a $\mathrm{II_c II_i I_l}$ point and is finite for $\mathrm{I_c II_i I_l}$ and $\mathrm{I_c I_i I_l}$ points.

4. Conclusions

A Lifshitz point exists in the A_2BX_4 compound at $c/a \sim 1.26$. This critical point is of a special type since three first-order transition lines meet at it. We suggest that this modification of the type of the Lifshitz point occurs because of the strong interaction with the elastic degrees of freedom. We now discuss briefly the further experimental developments that can follow from the consideration given above.

- One can reach the Lifshitz point by means of a change of the factor c/a. This can be done e.g. by application of a uniaxial pressure along the c-axis in the compound K_2SeO_4 or Tl_2SeO_4 which has the appropriately small parameter $c/a = 1.27$. Another possibility would be the preparation of the solid solution $Rb_2W_xMo_{1-x}O_4$, continuously sweeping the ratio c/a from 1.27 at $x = 0$ to 1.25 at $x = 1$.
- The type of the Lifshitz point depends on the strength of the coupling constant γ^2/Cb. One can expect the coupling to reduce with the crystal elasticity and hence the Lifshitz point type to be modified by application of a hydrostatic pressure.
- A_2BX_4 crystals with similar c/a ratios should show similar behaviour. One can expect to discover a HT Inc phase in Rb_2ZnCl_4 ($c/a = 1.23$), in K_2CoCl_4 ($c/a = 1.24$), and in K_2CoBr_4 ($c/a = 1.24$). The study of the HT transitions of the crystals Rb_2ZnBr_4, Rb_2CoBr_4 and Rb_2ZnCl_4, with the ratio $c/a = 1.27$ which is very close to the critical Lifshitz value of 1.26, is therefore of special interest.

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