x-ray-diffraction study of a commensurate-incommensurate-commensurate phase-transition sequence in α-ZnP_2

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An x-ray-diffraction study has revealed an interesting sequence of phase transitions in α-ZnP_2. This sequence is shown to be related to the modulated structure—a soliton lattice—which has been found in α-ZnP_2.

1. Recent experiments have shown that in certain temperature and pressure ranges many crystals exhibit a spontaneous periodic modulation[1] with a period which sometimes is and sometimes is not a multiple of the period of the original lattice (commensurate and incommensurate phases, respectively). The problem of incommensurate phases and of phase transitions between commensurate and incommensurate phases has recently become the subject of active research.[2,3] In most cases, the transitions from a commensurate phase to an incommensurate one occur through the formation of a regular array of domain walls (solitons) of insignificant width l_0, which separate nearly commensurate regions.[4,5] The primary motivation for the research on these transitions is that there are still unanswered questions regarding the mechanism for the formation of solitons, their dynamic characteristics, and their structural characteristics. In this letter we report experimental results on phase transitions and modulated structures (solitons) which have been found in α-ZnP_2.

2. In a detailed x-ray-diffraction study of α-ZnP_2 single crystals we observed an unusual sequence of phase transitions (Fig. 1). On the temperature dependence of the

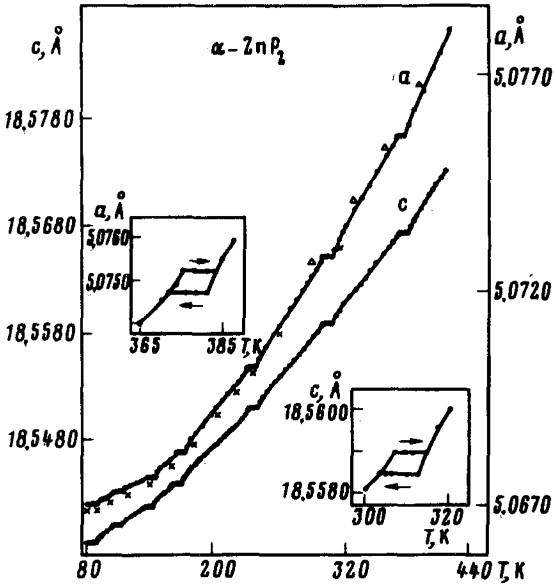

FIG. 1. Temperature dependence of the lattice constants of tetragonal ZnP_2. ×—Data of Ref. 13; Δ—data of Ref. 12.

lattice constants these transitions are seen as double jogs, between which the lattice constants do not change; the intensities of the structural features in the x-ray diffraction pattern go through minima at the anomalous points (Fig. 2). There is a slight hysteresis (Fig. 1). We have observed similar phase transitions in monoclinic β-ZnP_2. In terms of the temperature dependence of the lattice constants, the phase transitions observed in α-ZnP_2 resemble second-order transitions; on the other hand, the transi-

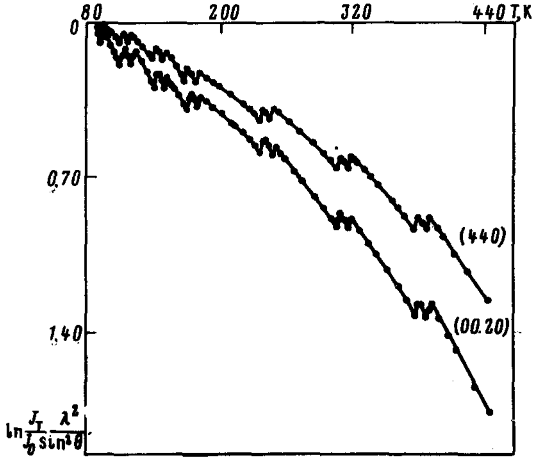

FIG. 2. Temperature dependence of $(\ln J_T/J_0)(\lambda^2/\sin^2\theta)$ for the (440) and (00.20) reflections of α-ZnP_2.

tions are accompanied by a significant hysteresis which would be chracteristic of a first-order phase transition. Under the circumstances, we cannot definitely classify these transitions as either first-order or second-order. Recent experiments have revealed entities that behave in a similar way.[7,8] At these transitions the order parameter and associated properties change discontinuously, while the phase transition is accompanied by a significant hysteresis. Although these results have yet to be explained, the universal manifestation of this behavior has led Unruh[4] to suggest that it is a common property of transitions between commensurate and incommensurate phases. Analysis of the anomalies in the properties which we measured thus suggests that the phase transitions in α-ZnP_2 result from a succession of superstructures which go through an incommensurate state. To test this possibility we have carried out a search for modulated structures.

3. The apparatus and goniometer described in Ref. 6 were used for the x-ray study of the superstructure. The sensitivity of the apparatus is 3–10 counts/s. This sensitivity is good enough to reveal the 001, 002, 003, 005, 006, 007, 009, 00.10, 00.11, 00.13, 00.15, 00.17, 00.18, and 00.19 reflections form the $00l$ plane in α-ZnP_2. These reflections are forbidden in this structure by the fourfold helical symmetry. Near the forbidden reflections with even indices we observe some additional superstructural reflections. We typically observe a slight splitting of these reflections. To determine the nature of these superstructural reflections, we studied the temperature dependence of their positions and their integrated intensities over the temperature range 80–500 K at a step ~3 K. Figure 3 shows the temperature dependence of the integrated intensity of

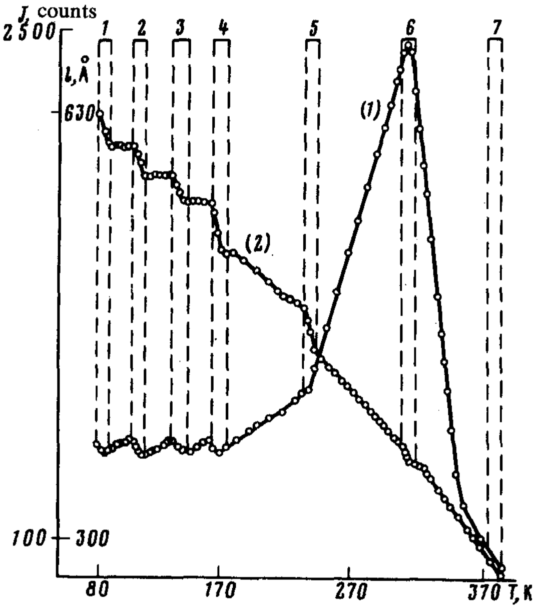

FIG. 3. 1—Temperature dependence of the integrated intensity of the superstructural reflections of tetragonal ZnP_2; 2—temperature dependence of the superstructure modulation period of this material. Areas 1, 2, 3, 4, 5, 6, and 7 correspond to temperature regions in which the lattice constant of α-ZnP_2 does not change.

the superstructural reflection and of the modulation period of the superstructure, calculated from the expression[9] $\Delta\theta = \lambda/2l\cos\theta$. It can be seen from Fig. 3 that the modulation period of the superstructure decreases with the temperature, and the temperature regions in which the jog anomalies are seen in the $l = f(T)$, $J_{\text{SSR}} = f(T)$ curves are the same as the temperature regions in which the anomalies are seen on the temperature dependence of the lattice constants of α-ZnP_2. The implication is that the phase transitions observed in α-ZnP_2 are due to a modulated structure which disappears at $T \sim 385$ K. The very large modulation period ($l = 630$ Å at $T = 80$ K) is characteristic of a lattice of solitons[10]; the intensification of the superstructural reflections in the temperature region 172–307 K can be attributed to an increase in the density of solitons,[11] while the sharp decay (Fig. 3) can be attributed to a breakup of the soliton lattice.

4. Analysis of the temperature dependences $l(T)$ and $J_{\text{SSR}}(T)$ leads to the following conclusions.

a) In the regions between areas 1, 2, 3 and 4 (Fig. 3) there exists a commensurate phase in which solitons are pinned by a Peierls barrier,[3] and the distance between solitons does not change (Fig. 3). The intensification of the superstructural reflections in these regions is probably due to an increase in the dimensions of the solitons.[3,11]

b) In areas 1, 2, 3 and 4 there exists an incommensurate phase in which solitons are not pinned.[2,3,11] Within these regions, we observe a decrease in the distance between solitons (i.e., a decrease in the period of the superstructure) and, correspondingly, an increase in the density of solitons with increasing temperature.

c) Working from the definition of the "devil's staircase,"[1–3] we might suggest that there is an incomplete devil's staircase in the temperature range 80–172 K, since transitions between commensurate phases do not occur abruptly but through an incommensurate state, which fills a temperature interval ~8 K wide.

d) In the temperature regions between areas 4, 5, 6, and 7 there is a smooth decrease in the period of the superstructure, in contrast with the regions discussed above, where the modulation period does not change. In this case there is again a commensurate state in these regions, but here the region in which $l(TY)$ changes is a succession of discrete commensurate configurations between which transitions occur only after surmounting potential barriers. It may be that there is a complete devil's staircase in such regions.[3]

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