Induction of an incommensurate state by a periodically varying temperature field

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Observations reveal that a phase transition to an incommensurate phase can occur not only as the temperature (or the pressure or a field) is varied but also during the application of a periodically varying temperature field. It has been found that a periodically varying temperature field exhibits the properties of an external inducing agent which gives rise to an incommensurate structure. The relationship between the periodic temperature field and the incommensurate effects is discussed.

A common feature of incommensurate crystals is the following sequence of phases as the temperature is lowered: (normal phase, *P*)-(incommensurate phase, *I*)-(commensurate phase, *C*).[1] In most cases the external agent is the temperature (in rare cases it is the pressure or a field). No other methods for inducing an incommensurate state in a solid have been identified so far. Two-dimensional systems (adsorbed films) are exceptions to this statement; in them, a transition to an *I* phase can occur upon a change in the degree of surface coverage.[2]

We have observed that an incommensurate state can be induced in crystals of $Li_2B_4O_7$ (TBL) by an unusual external agent: a periodically varying temperature field. We have also observed that the phase transition to the *I* phase depends on the shape of this external agent. On the Laue and other x-ray diffraction patterns of "fresh"[1] crystals there no superstructural reflections. The implication is that there is no incommensurate modulation (the crystal is in the normal state). If the crystal is instead subjected to a cyclic heat treatment as described in Fig. 1a, satellites appear on the Laue and

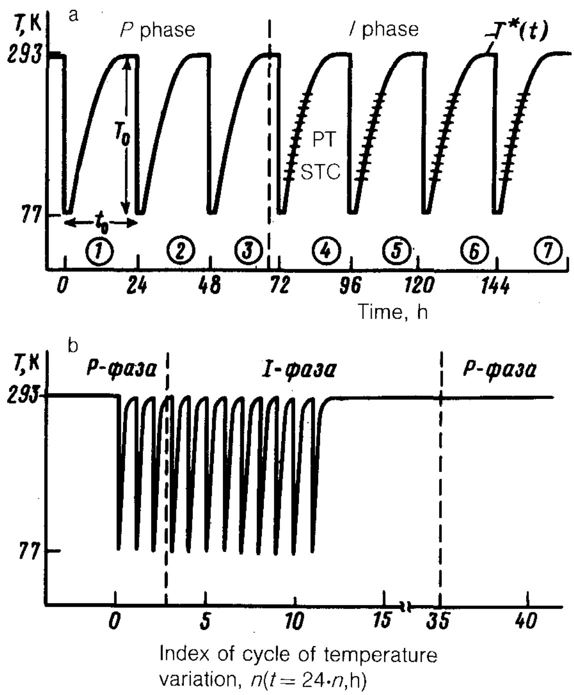

FIG. 1. a: Time evolution of the temperature field around the sample and *P-I* structural phase transition in an $Li_2B_4O_7$ (TBL) crystal as the index (n) of the cycle of the periodic temperature variation changes. The barred regions show the temperature region in which the phase transitions stimulated by the thermal cycling (PT STC) are observed; the numbers in circles show the index of the cycle ($T_0 = 216$ K, $t_0 = 24$ h). b: Periodically varying temperature field in which a *P-I-P* sequence of phase transitions is observed in TBL.

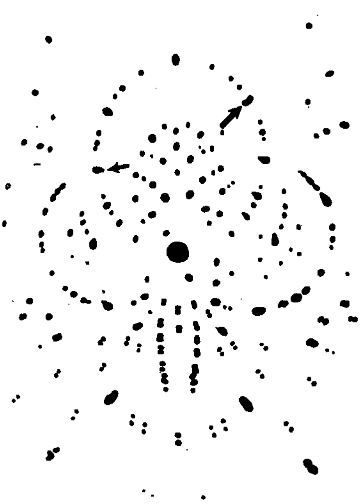

FIG. 2. Laue pattern of a TBL crystal after application of a periodically varying temperature field (the arrows mark satellites).

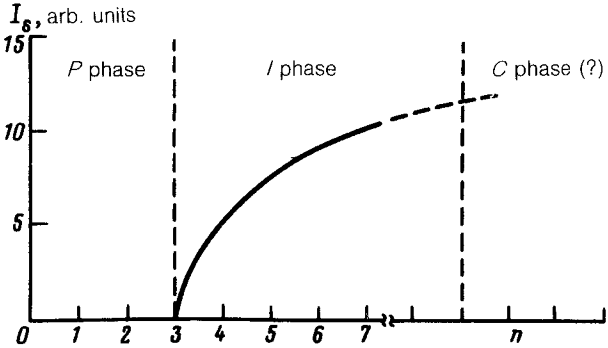

FIG. 3. Intensity of a satellite versus the index of the cycle of the temperature variation.

other x-ray diffraction patterns (Fig. 2). The time evolution of the temperature field around the crystal is shown in Fig. 1a: $T^*(t) = f(t)$, where $T^*(t)$ is a periodically varying temperature field which may be thought of as a special external agent which induces an incommensurate state. The basic characteristics of this agent are (Fig. 1a) T_0, which is the amplitude of the periodically-varying temperature field; T_0, which is the period of this field; and n, which is the order of the cycle in the variation. In the TBL crystals, the phase transition to the I phase (the P-I transition) occurs at $n \geqslant 3$ (Fig. 3) for the given field $T^*(t)$ (Fig. 1a). This fact is established by the appearance of satellites on the Laue patterns (Fig. 2). The particular value of n depends on the shape of the function $T^*(t)$. The intensity of the satellites which appear increases with increasing n. We have not yet studied the processes by which the I phase of TBL is transformed as a function of n, but we do not rule out the possibility that at larger values of n there may be a phase transition to a commensurate phase (Fig. 3). When the periodic variation of the temperature field is stopped $[T^*(t) = T_{\text{room}} = \text{const}]$, the crystal relaxes (over a time $t = nt_0 = 20$ days, for $n = 20$) to its normal state; i.e., the I-P phase transition occurs (Fig. 1b). Consequently, the following sequence of phases is observed for TBL crystals subjected to the varying temperature field $T^*(t)$ described by the function in Fig. 1b: P-I-P.

The relaxation nature of the I-P phase transition is evidence of a possible participation of the defect subsystem of the crystal (vacancy voids, dislocations, vacancies, etc.) in the formation of an incommensurate structure constituting a spatial ordering of defects.[2] An incommensurate modulation of the defect structure (in contrast with a modulation of the crystal lattice) is a new type of incommensurate state: a "defect" superstructure. Induced by an external agent, specifically, by the periodically varying temperature field, this superstructure strongly influences the physical properties of the crystal. These properties can be controlled by varying the nature of the external agent $[T^*(t), t_0, T_0,$ and $n]$. For example, in the TBL crystals we observe an unusual sequence of phase transitions, in a number which depends on the index of the cycle of the periodically varying temperature field.[3] A distinctive feature of the crystals with a defect I phase, which distinguishes them from ordinary incommensurate crystals, may be the absence of P-I and I-C phase transitions as the temperature is varied from 0 K to T_m. Evidence for this conclusion comes from the very broad temperature region in which the I phase exists in TBL (Ref. 3). Ignoring the effect of a periodically varying temperature field will unavoidably lead to ambiguities in experimental results.

Note that all of the crystals "react" to the agent $T^*(t)$ to some extent. We call those crystals whose physical properties depend strongly on $T^*(t)$ "PVTF crystals" (from "periodically varying temperature field"). There may be high-temperature superconductors in this group. Recent experiments indicate that the formation of incommensurate structures in high-temperature superconductors and the subsequent evolution of these structures in a periodically varying temperature field correlate with the superconducting characteristics (state) of the samples. This fact suggests that incommensurate defect superstructures may be involved in the mechanism for high-temperature superconductivity.

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[1)]Crystals which had not been used for a study of temperature-induced effects and which had not been subjected to heat treatment.

[2)]There are other facts which point to a modulation of defects: 1) the very low intensity of the satellites (I_s is three or four orders of magnitude below I_B); 2) the weak temperature dependence of I_s.

[1]R. Blinc and A. P. Levanyuk, *Incommensurate Phases in Dielectrics,* North-Holland, Amsterdam, 1986, p. 402.

[2]I. F. Lyuksyutov, Ukr. Fiz. Zh. **28**, 1281 (1983).

[3]V. V. Zaretskiĭ and Ya. V. Burak, Pis'ma Zh. Eksp. Teor. Fiz. **49**, 198 (1989) [JETP Lett. **49**, 229 (1989)].

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