Self-oscillatory regime of ferroelectric phase transition in proustite under continuous illumination

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Periodic structural rearrangements of the para-ferro-para states are observed in nonlinear crystals of proustite under steady-state conditions of thermostatic control and continuous optical pumping.

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At 28 K trigonal proustite crystals (Ag_3AsS_3) undergo phase transition of the first kind to a ferroelectric state with a lowering of symmetry to triclinic. Moreover, it was established that the photosensitivity of proustite determines a noticeable narrowing of the temperature hysteresis provided that the phase transition occurs in illuminated conditions.[1,2]

In this work we show that we do not register some given phase transition in the case of continuous optical pumping at a constant temperature, but instead we observe an effect of a periodic recurrence of para-ferro-para states.

The basis of the x-ray-diffractometric method[1)] is the continuous recording of the integral intensity I of selected reflections of one of the phases. Since phase conversion entails displacement or splitting of the diffraction peak, a decrease in intensity I is an indication of structural rearrangement and the restoration to the initial level indicates a reverse transition.

In the absence of special bias lighting in the region of phase conversion the temperature dependence of the intensity follows a conventional hysteresis loop (Fig. 1a). When illuminated on the order of 10^3–10^5 lux, the loop width is considerably narrowed (Fig. 1b). Beginning at the 10^6-lux level, hysteresis was practically eliminated and at subsequently higher illumination levels we observed stable intensity oscillations

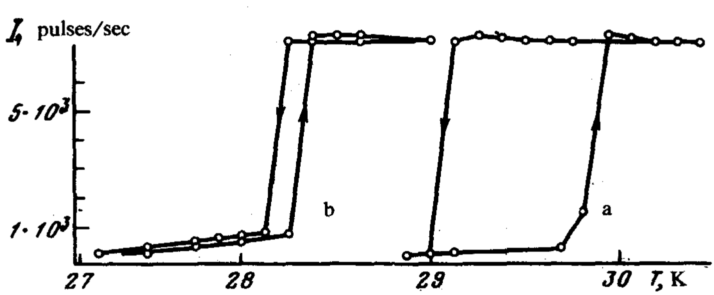

FIG. 1. Temperature variation of the integral intensity of diffraction reflection (006) of the para-phase: a—without illumination; b—with illumination $E \approx 5\times10^5$ lux.

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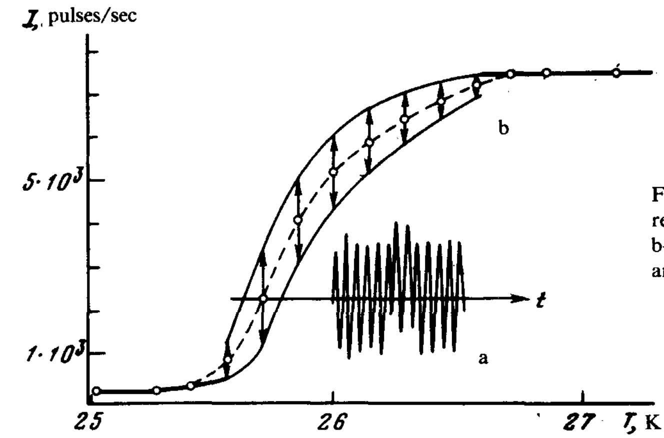

FIG. 2. a—Oscillations of intensity reflection (006) at fixed temperature; b—temperature dependence of the amplitude of intensity oscillations.

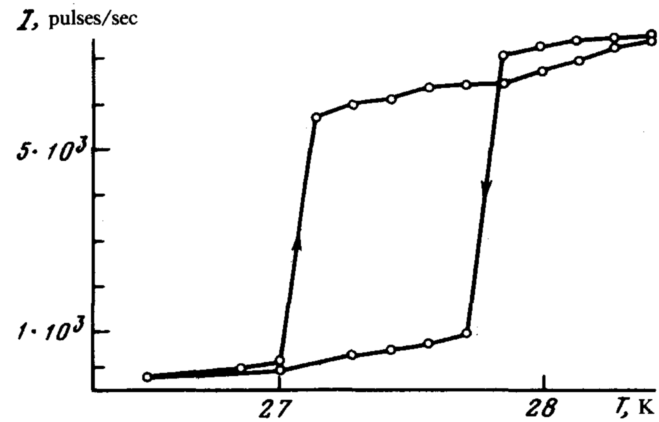

FIG. 3. Variation of intensity (006) recorded at $E = 1.5\times10^6$ lux in the temperature drift regime ≈ 0.3 deg/sec.

of the x-ray diffraction peak which indicate a periodic rearrangement of the crystalline structure. The time for one cycle of a reversible rearrangement was ~ 1.5 sec. As an example, Fig. 2a shows the time dependence of integral intensity for the reflection (006) of a high-temperature phase. The self-oscillatory regime of the phase transition is preserved in a given temperature interval whose width increases with illumination. Figure 2b shows an example of the temperature dependence of amplitude of intensity oscillations under an illumination of $\sim 1.5\times10^6$ lux.

In order to interpret these results we shall focus on the fact that because of the unique nonlinear properties of proustite ($d_{22}\,Ag_3AsS_3 \approx 60\cdot d_{31}$ KDP [4]) considerable optical detection should occur even when conventional light sources are used. Thus, in view of the small values of spontaneous polarization ($P_s = 2\times10^{-2}$ mcoulomb/cm^2 [5]), intensive pumping of proustite may stimulate transition into a ferro-phase due to detection in a manner similar to the effect of a static electric field. It is also known that considerable changes in nonlinear characteristics may also be observed when a phase transition occurs. Thus, for $BaTiO_3$ it was established that the second harmonic intensity increases significantly at the point of ferroelectric transition.[6] Unfortunately, the nonlinear characteristics of proustite at low temperatures have not been studied. However, our results may be used to propose that the nonlinear coefficient in the ferro-phase decreases considerably in the axial direction of spontaneous polarization ($P_s \| [10\bar{1}0]$). Actually, the occurrence of a ferroelectric state under this condition is accompanied by a reduction of the constant component of polarization as a result of which the structure of low-temperature phase becomes unstable and the crystal undergoes a reverse phase transition. Subsequently, the entire sequence is repeated since some nonlinear properties are restored in the high-temperature phase which determine the stimulating effect of light, etc. The characteristic time (~ 1.5 sec) in this cyclical process is evidently associated with the real inertia of the structural transformations and not with electronic processes which determine the nonlinearity of a material.

The observed instability is also confirmed in experiments carried out under conditions of temperature drift. In this case an unusual situation of rotation of the hysteresis loop may be effected (Fig. 3) if the time a crystal remains at each temperature point is shorter than the period of the self-oscillatory process.

[1)] In this experiment we used: the DRON-1.0 X-ray camera, CuK_α-emission, a thermostat designed by A.A. Boĭko and V.S. Medvedev,[3] and the DKsSh-120 high-pressure xenon lamp.

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