

Laser-induced structural phase transition in a PbI_2 single crystal

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A structural phase transition between polymorphic modifications of a layered PbI_2 crystal has been induced at room temperature by a laser beam for the first time. The transition is from a state with a higher free energy to one with a lower free energy.

Layered structures such as PbI_2 exhibit a polymorphism, i.e., an ability to crystallize in different polymorphic modifications: $2H$, $4H$, $6R$, etc. In the present letter we are concerned with the phase transition between the $2H$ and $4H$ polymorphs.¹⁾ The difference between the crystal structures of these two polymorphs lies in the order in which the layer packets alternate (the layer packet in PbI_2 is formed by three monolayers: I-Pb-I), while the structure of the layer packets themselves remains the same. All the layer packets in the $2H$ - PbI_2 lattice are translationally equivalent, while in $4H$ - PbI_2 each third packet occupies a position equivalent to that of the first packet, while the second is displaced slightly and rotated through 180° with respect to the others. The interaction between packets in PbI_2 is weak and determined primarily by van der Waals bonds.

From the thermodynamic standpoint the polymorphism of PbI_2 is determined by a difference in the temperature dependence of the free-energy curves of the different polymorphs. The point at which these curves intersect is the phase-transition point. Each polymorph can exist as a stable or metastable phase on each side of the transition point. For example, the stable polymorph in PbI_2 below the phase transition point ($T = 450$ K; Ref. 1) is the crystal structure of the $2H$ polymorph; the $4H$ structure is a stable high-temperature polymorph before the transition to the region in which the next higher-temperature polymorph, $6R$, exists stably; etc. A temperature-induced phase transition is a common effect. In the present letter, on the other hand, we wish to discuss a new effect: a $4H \rightarrow 2H$ conversion in PbI_2 induced by laser light at room temperature.

The test samples were $2H$ - PbI_2 and $4H$ - PbI_2 single crystals originally grown in these polymorphs. The crystals were bombarded at 273 K by pulses from a ruby laser (this light is absorbed weakly; $h\nu < E_g$) in free-running operation ($\tau = 6 \times 10^{-3}$ s, $E = 2$ J). The beam is focused into a spot 4 mm on the sample. The structural polymorph is identified by a standard procedure through an analysis of the exciton reflection spectra [$R(\lambda)$] recorded at 4.2 K. This particular method was chosen because of the exceptional sensitivity of the $R(\lambda)$ spectra to structural changes in the crystal.

Although the results reported here (Fig. 1) were obtained from three PbI_2 samples, they are representative of all the more than ten $2H$ and $4H$ crystals which we studied. 1) After bombardment of the $4H$ - PbI_2 crystals by five pulses, a structure corresponding to an exciton state of the $2H$ polymorph appears in the $R(\lambda)$ spectra

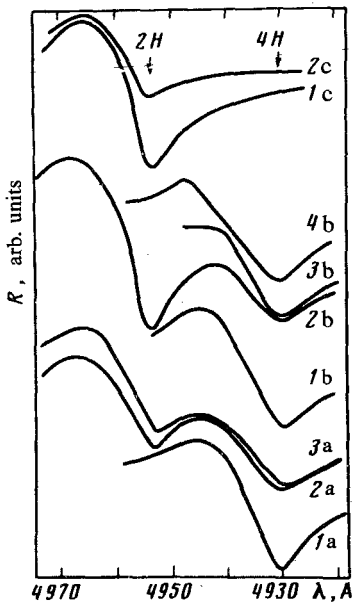


FIG. 1. Reflection spectra of two $4H$ - PbI_2 samples (curves a and b) and of one $2H$ - PbI_2 sample (curves c) at 4.2 K. 1a-1c—Initial states; 2a-2c—after bombardment by five laser pulses; 3a—6 months after bombardment; 3b—backside of the bombarded crystal; 4b—after removal of a surface layer from the bombarded side. The curves have been separated from each other by arbitrary distances along the ordinate axis.

measured on the side of the bombarded surface (curves 2a and 2b in Fig. 1). We were not able to obtain a complete conversion of the $4H$ polymorph into $2H$ either by raising the power in the pulse or by increasing the number of pulses up to the point at which the crystal was destroyed. 2) In order to follow the time evolution of the degradation of the $R(\lambda)$ spectrum we repeated the measurements of $R(\lambda)$ 6 months after bombardment. In the interim the crystal had been left in darkness at room temperature. We found no changes in the $R(\lambda)$ spectrum over this period (curve 3a in Fig. 1). 3) After a surface layer was removed from the bombarded surface of the crystal, the $R(\lambda)$ spectrum was found to be identical to the original spectrum (curve 4b in Fig. 1); i.e., the spectrum was found to correspond to the $4H$ polymorph. The thickness of the layer in which the $4H \rightarrow 2H$ transition occurs is no greater than 10–30 μm . On the opposite side of the crystal ($d \sim 1$ mm), where the laser beam exited, we do not observe a structure in the $R(\lambda)$ spectrum corresponding to the $2H$ polymorph (curve 3b in Fig. 1). This result implies that the $4H \rightarrow 2H$ structural conversion due to the laser bombardment occurs exclusively at the bombarded surface. 4) A similar laser bombardment of the $2H$ - PbI_2 crystal did not reveal a $2H \rightarrow 4H$ transition (curve 2c in Fig. 1).

Let us discuss the results. As mentioned earlier, the crystal structure of the $2H$ polymorph is a stable low-temperature modification. It corresponds to an absolute minimum of the free energy (U). The structure of the $4H$ polymorph is, in contrast, a metastable modification (curve 1 in Fig. 2). The polymorphic conversion $4H \rightarrow 2H$ can be achieved only by overcoming an energy barrier, because the structure must go through some energetically unfavorable intermediate states with an elevated free ener-

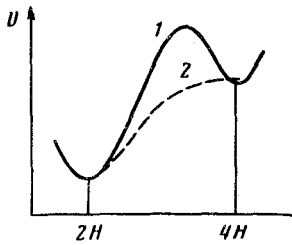


FIG. 2. Schematic diagram of the free energy of the PbI_2 crystal versus the arrangement of its atoms. Solid curve—energy relief under normal conditions; dashed curve—in a laser beam.

gy. In principle, this transition can occur as a result of thermal fluctuations, but at low temperatures this would be improbable because of the low probabilities for the corresponding high-energy fluctuations. As a result, the less stable $4H$ modification exists for a long time (years) in the metastable state. In the field of a laser beam, on the other hand, the $4H \rightarrow 2H$ transition occurs in a fraction of a second. The high rate of the phase transition indicates that the energy barrier in the reaction path is removed, i.e., that the phase transition is nonthermal. Consequently, the free energy of a PbI_2 crystal in the field of a laser beam can be represented by curve 2 in Fig. 2. In a sense, the effect of the laser beam, which eliminates the energy barrier, can be compared with the effect of a catalyst which promotes various polymorphic conversions.

The first step of the phase transition thus corresponds to a transition of the original $4H$ polymorph in the laser light into an absolutely unstable (labile) state, from which there is a spontaneous relaxation to an energetically preferred structural state (the $2H$ polymorph). The inverse transition, $2H \rightarrow 4H$, cannot occur even in the laser beam, as can be seen from curve 2 in Fig. 2, since only the $4H$ polymorph becomes unstable; the $2H$ polymorph again corresponds to the most favorable state from the energy standpoint. Furthermore, the $2H \rightarrow 4H$ transition requires an expenditure of energy. We thus see why we do not observe the $2H \rightarrow 4H$ phase transition in the laser beam.

Unfortunately, we cannot draw a definite conclusion at this point regarding the mechanism by which the laser beam puts the $4H$ polymorph in a labile state or regarding the localization of the phase transition near the surface. These questions require further experimental research.

We would like to point out an analogy between this structural transition and laser annealing,² in which, in particular, there can be a transition from an amorphous state to a crystalline state, i.e., a transition from a state with a relatively high free energy to a state with a relatively low free energy, as in the case under study here.

¹The symmetry of the crystal structures of the $2H$ and $4H$ polymorphs is described by the space groups D_{3d}^3 and C_{3v}^2 , respectively.

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