*Structure, defects and phase transitions in the III group monohalides

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Abstract

The influence of the defect subsystem on the exhibition of incommensurate phase in crystals of halides of metals of the third group was investigated. The correlation has been found between the quality of specimens and the incommensurate parameter. The nature of chemical bonding and aspects of structural disordering are discussed.

Introduction

Layered crystals of metals of the third group (InI, InBr, TlI, InCl) are the typical compounds of A^3B^7 family with pronounced anisotropy of crystal structure and optical properties. It is substantial that the similar two-dimension structures are in the greatest degree apt to the appearance of various perturbations in the translational symmetry which count on both presence of defects, dislocations and vacancies, and directed effect of exterior variables. Such violations of symmetry produce the re-orientation of clusters and this, in other turn, causes the asymmetric disturbance to impose upon the centrosymmetric component. The detection of the low-temperature phase transitions in these compounds [1] makes them attractive objects for studying and building phase transition models in strongly anisotropic media.

The aim of the present paper is to investigate the influence of defects and structural disordering on the properties of compounds with space group D_{2h}^{17} *(CmCm)*, in which both local and macroscopic components have central symmetry. For the investigations single crystal specimens of indium iodide and indium bromide were used. These crystals crystallize as layered structures only, unlike TiI and InCI that may also have simple cubic structure [2].

Experimental

Indium bromide was obtained using chemical reaction between metallic indium and liquid brom in vacuum with excess of indium for preventing formation of $InBr_3$. Indium iodide was synthesized in a similar way.

The single crystals were grown by the Bridgman method after distillation in vacuum (10^{-6} torr) and zone refining in helium atmosphere (approximately 100 torr). The boules obtained were easily split perpendicularly to *y*-axis, the obtained specimens had the mirror surfaces of high quality in *ac*-plane and didn't need any further polishing.

Structural parameters of single crystals were verified using X-ray diffractometer "DRON-05". Temperature investigations were done in the interval 4.2-500 K with the stabilization of 0.1-0.2 min.

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*This article is published as an exception as it doesn't suit to the demands of the UJPO but it corresponds to the materials of the First Ukrainian Workshop of Ferroelectrics and Related Materials

The Senarmon method ($\lambda = 0.6328\mu m$) was used for the determination of piezooptical constants. The spontaneous polarization was controlled by the Soyer-Tower method ($f = 10$ Hz, $E \leq 10^6$ V/m, $\Delta P_{spont} = 2 \cdot 10^{-4}$ $\mu C/cm^2$).

The quality of InI and InBr specimens was diagnosed by the method of X-ray study. It enables us to choose samples of various structural perfection, which were characterized by defectiveness parameter ξ that was defined as a ratio of the diameter of ion reflexes in the most perfect specimens to the diameter of blurred reflexes. The determination of the defectiveness parameter in such a way is well justified for the layered compounds with the great anisotropy of chemical bond [3]. In a similar fashion the samples with values of defectiveness in the range from 0.36 to 1.0 were detected. The certain number of specimens of poor quality had to be annealed in the non-inertial medium under the temperature of 355 K.

Results and discussions

The temperature investigations allowed us to reveal simultaneous coexistence of two structural phases in the region of temperatures below 25 K. The first phase belongs to the space group D_{2h}^{17}, and the second one was identified as acentric C_{2v}^{9} phase. At the phase transition point an orthorhombic crystal with a point symmetry group *mmm* undergoes a distortion. The distortion consists in the homogeneous shift deformation of the elementary cells along *z*-axis, the lattice symmetry reduces to *mm2*. At that all the symmetry elements disappear except for the axis 2 (along *z*-axis) and the symmetry planes that are parallel to it. In case of InBr single crystals the effect being watched exhibits itself significantly weaker than for InI.

The behaviour of incommensurate parameter that was determined from X-ray satellite reflexes for samples with different quality is shown in figure 1. The improvement of

the quality of single crystals was accompanied by both narrowing of the temperature interval of incommensurate phase existence and reduction of the superstructure modulation.
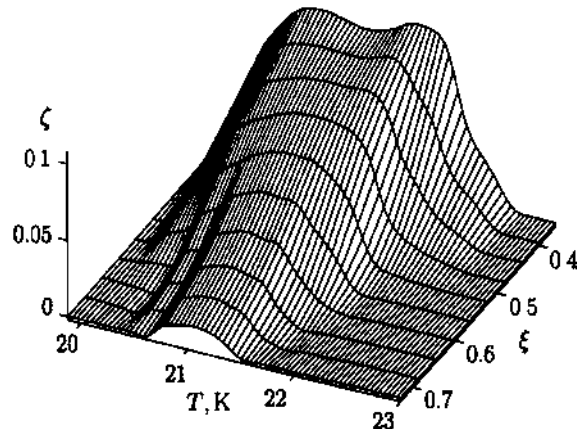

Fig.1. The effect of the defectiveness of crystals ξ upon the temperature and incommensurate parameter ζ.

The monohalides of metals of the third group have a layered structure with the layers, parallel to *ac*-plane. The unit cell of the compounds containing four formula units is shown in figure 2. Each layer which consists of two sublayers seems to be the packet of the compound molecules that is oriented parallel to *b* axis and is shifted by *(a+b)/2* about the neighboring layers. The packet surface in the figure is gauffered because of bonding between metal atoms (*B* and *C* in figure 2) which belong to different layers. This bonding forms zigzag chains with short interaction distances. The TlI-type structure can be formally derived from layers of distorted version of NaCl structure each consisting of the plane grid of cation atoms and that of anion atoms which are mutually bound with bonds between nearest opposite atoms (i.e. *A-B* or *C-D*) in *y* direction. Apparently, the packet is thought to be one of the deformed CsCl-type with intrinsic cation-cation bonding when to consider it as formed by two adjacent planes of atoms (*C* and *D* in figure 2) which belong to different layers.
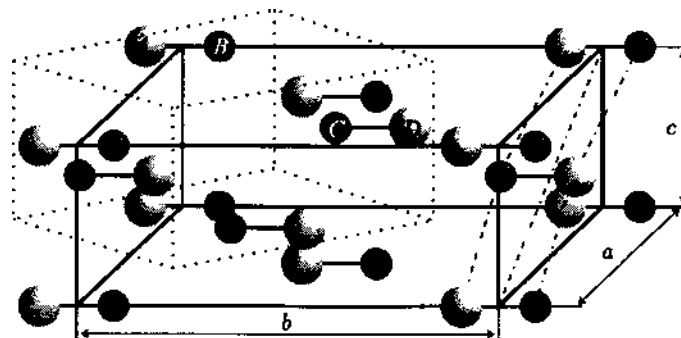
Fig. 2. Crystalline structure of compounds *CmCm.* Filled circles represent metal ions and open circles - halogen ions. The primitive cell is labelled by dotted lines and the corrugated surface of layered packets is shown by chain lines.

As it is shown in figure 3, a significant modulation was observed only along *z*-axis while parameters *a* and *b* are practically insensitive to the influence of structural disordering.

The electron charge distributions that has been calculated [5] using the norm-preserving nonlocal pseudopotential method [4] are shown in figure 4. Pseudotetragonal layers are oriented perpendicularly to *y*-axis in compounds with *CmCm* symmetry.

Such structure can originate from the rock-salt structure with shifted double layers of cations and anions perpendicularly to the fourfold axis. The contour for *bc*-plane shows that the modulation spreads along the weak, abnormally short by the distance between ions, cation-cation bond. This bond forms interlayer ordering in these "ten-electron" compounds with the "inertial s-electron pair" of the metal. The nature of the bonding between metal ions is

often substantiated by fluctuation-dipole forces. The instability of this bonding is proved also by numerical estimations:the binding interaction between two cations In^+ can arise in case when molecules are oriented by its cations toward each other and dimer is not linear (D_w) but has a zigzag symmetry group C_{2h}.

It should be noted that the calculation of atomic characteristics of these crystals produces distinctly larger broadening coefficients also for *z*-direction, it being known that the structural transition into cubic phase for TlI is observed when temperature increases and for InCl - when it drops.

The spontaneous polarization magnitude did not exceed $2\cdot10^{-4}$ $\mu C/cm^2$, which eliminates from consideration the idea about the ferroelectric origin of the transition. Instead in the region of temperatures 18-23 K the dilatometric investigations [1] proved the presence of spontaneous polarization. It is also worth to
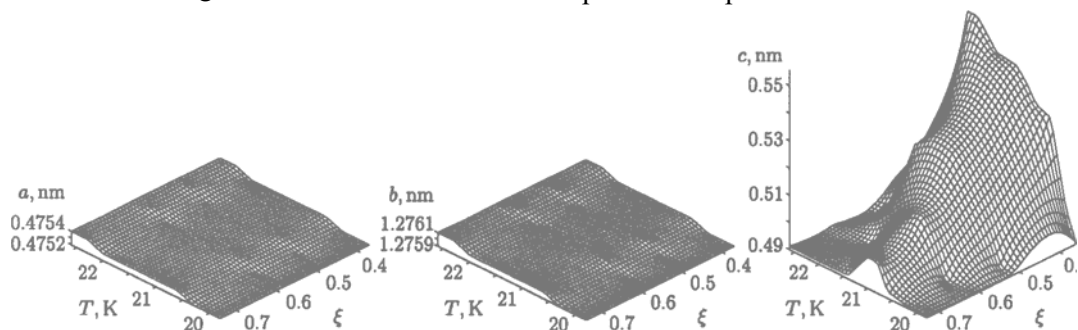

Fig.3. Dependence of temperature changes of lattice parameters of indium iodide in the vicinity of phase transition point on the quality of specimens.
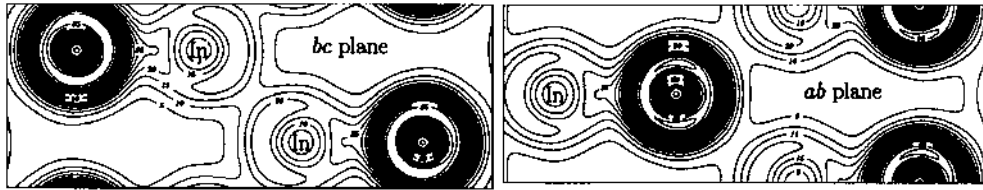
Fig.4. Electron density distribution in single crystals InI in *bc* and *ab* planes. Results are given in electron/cell (normalized to unity).

remark that the absolute values of U_{xy} suffer changes (up to 15-25%) under the influence of both neutron radiation and oxidation of the surface. On the basis of these data we make conclusion about the ferroelastic classification of the discussed transition. The study of the behaviour of piezooptical constants π_{2222} and π_{3333} has demonstrated their substantial difference. The last one did not depend on temperature whereas π_{2222} underwent the considerable changes, as it is shown in figure 5.
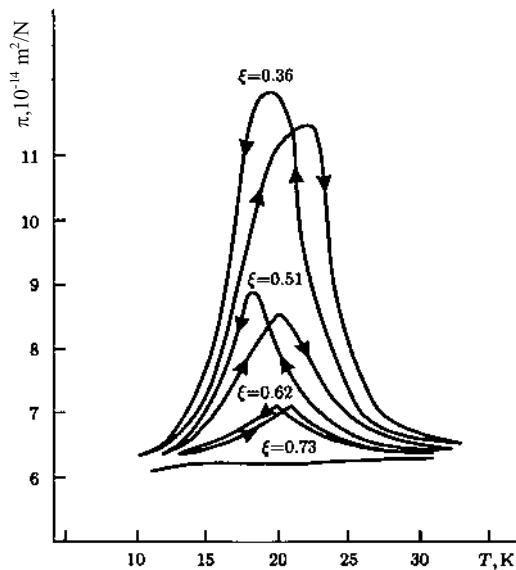

Fig.5. The temperature hysteresis of the piezooptical π_{2222} constants for InI single crystals of different sample perfection ξ.

In fact, the reduction in the quality of specimens was accompanied by the increase of the absolute π_{2222} value and by broadening of the temperature interval of existence of incommensurate phase along with the hysteresis increase.

The appearance of the acentric phase was also observed after radiation processing of the perfect specimens with α-particles of isotope californium-252 [6]. In that case the measured values of components of electrooptical tensor were two orders less than in the typical electrooptical crystals, though they were in strong correlation with the structural data. This validates the interlayer origin of the phenomenon.

Acknowledgements

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