Isostructural phase transition in $In_xTl_{1-x}J$ system

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Abstract

The infrared absorption spectra of the $In_xTl_{1-x}J$ -system layered crystals are studied. The essential changes in their structure are observed, depending on the content of thallium component. These changes are related to isostructural phase transition. A role of free charges in the structural transformations is discussed.

Keywords: layered crystals, infrared spectroscopy, transmittance spectra, isostructural phase transition.

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Introduction

The problem of solid solubility attracts much attention of researchers and technologists, since the parameters of materials can be controlled by the changing of the content of solutions. By changing the thallium Tl content in the $In_xTl_{1-x}J$ lattice, we have revealed a formation of intermediate phase characterized by specific changes in the distribution of thallium component. Moreover, the X-ray structure investigations have shown that the lattice symmetry does not change [1], i.e. we deal with an isostructural second-order phase transition.

The $In_xTl_{1-x}J$ system at $(1-x)\leq 0.3$ can certainly be considered as a substitution-type solid solution because the lattices of both InJ and TlJ components are described in terms of the same nonsymorphous symmetry group D_{2h}^{17}=Cmcm, while the ionic radii of In^+ and Tl^+ differ less than 15%. The structures of both compounds are layered, with the two layers of a sandwich type in the elementary cell and four formula units in the cell. The layers are oriented perpendicular to the crystallographical **b** axis (Fig.1). The lattice parameters depend on the content of the solid solution [2].

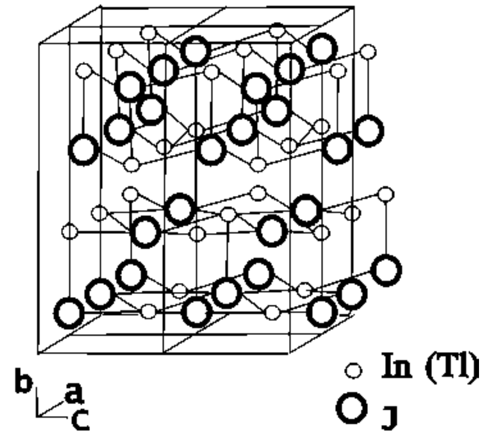

Fig.1. Crystal lattice of the orthorhombic modifications of InJ and TlJ. The larger balls represent the anions and the smaller the cations.

The coordination numbers equal to 7 (Fig.2) are characteristic for the structures of this type, so that they represent an intermediate case between the NaCl-type (space group O_h^5=Fm3m, the coordination number 6) and the CsCl-type (space group O_h^1=Pm3m, the coordination number 8) structures. The local symmetry of cations and anions corresponds to the point group C_{2v} = mm2. The unit cell contains two formula units.

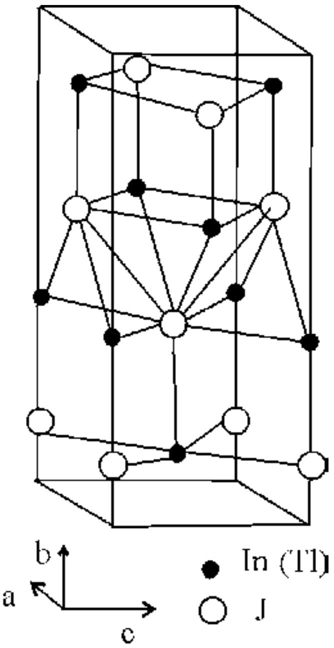

Fig.2. Arrangement of atoms in the lattices of α-TlJ.

The solution of the charge density distribution function [1] testify that the chemical bonds within the layers of the orbit lattices of InJ and TlJ have an ion-covalence character.

The subject of the present paper is to consider a special character of structural changes occurring in the layered crystals of the $In_xTl_{1-x}J$ system, ascertained by means of infrared (IR) spectroscopy, while changing the content of the system.

Experiment

Homogeneous samples with the average thicknesses 0.48 mm ÷1.8 mm and the cross section dimensions about 6×6 mm^2 with mirror-like, plane parallel surfaces, were obtained by cleaving the layered single blocks grown by the Bridgeman technique [1]. The plane of samples included the **a** and **c** axes.

The IR absorption spectra were studied with the Specord-80M apparatus characterized by the resolution of 0.1 cm^{-1}. The measurements were performed in the range of 200 to 1200 cm^{-1} at room temperature, using a polarized light.

The transmittance spectra T(ν) were measured on the polarizations **E**||**a** and **E**||**c**. Selenium was used as a polarizer.

The absorption coefficients were calculated by taking into account the reflection corrections according to the formula $K = \frac{1}{d} ln \frac{(1-R)^2}{T}$ where R denotes the reflection coefficient, d the sample thickness. The interference effects arising from the multiple reflection were not worth accounting for the samples of the above mentioned thicknesses.

The repeatedly performed spectra recordings always showed a reliable reproducibility of their structure.

Structure of the IR absorption spectra

The IR absorption spectra for the four $In_xTl_{1-x}J$ samples with different content of the components detected in the case of the **E**||**c** polarization are depicted in Fig.3a–d. In order to analyze the structure of the spectra, we have distinguished five characteristic regions where peculiar changes dependent on x are observed. Let us consider them in greater detail. The system of bands I in the region 960-1100 cm^{-1} is associated with the InJ sublattice vibrations.

These bands "extinct" with decreasing In content and practically disappear at x<0.5. The disappearing seems to be surprising enough, if one takes into account only the dependence on the In^+ ion concentration. As seen from the following discussion, the absorption of free charges is essential in the phenomenon. The intensity band at 708 cm^{-1} (the region II) is sensitive to the Tl^+ concentration.

The system of broad bands at ν<600 cm^{-1} abbreviated as M, is transformed to a single broad band that almost does not posses inferior structure when the thallium content increases. We relate the nature of the last band to the transitions among the subbands (Fig.4).

Making such transitions possible in the experiment using no extra irradiation with high-energy quanta ($h\nu>=E_g$) is a non-trivial phenomenon. The transitions among the valence sub-bands (ΔE~0.065 eV) are caused by the hole concentration increasing at (1-x)≥0.3, when some fraction of thallium ions become located in the inter-layer gaps. A qualitative confirmation

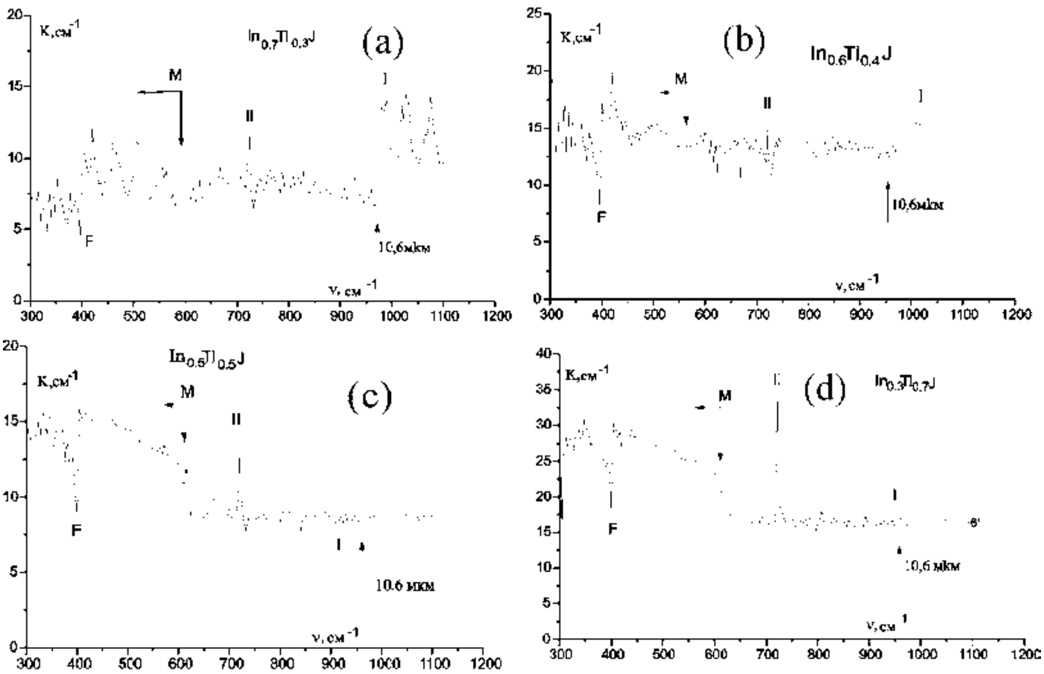

Fig.3. IR absorption spectra for $In_xTl_{1-x}J$ at x=0.7 (a), 0.6 (b), 0.5 (c) and 0.3 (d).

of such a tendency is an increase in the background absorption at the CO_2 laser radiation wavelength (λ=10.6 μm). It is known that the free charge absorption coefficient

$$K_{\text{f.c.}} \cong \frac{\varepsilon_\infty \omega_p^2}{nc\omega^2\tau}; \text{ where } \omega_p^2 = \frac{Ne^2}{\varepsilon_0\varepsilon_\infty m^*}, \text{ i.e.}$$

$$K_{\text{f.c.}} \sim N(\omega^2 m^* \tau)^{-1}.$$

Table 1. Change of absorption at λ=10.6 μm dependent upon the content of thallium component in the system of $In_xTl_{1-x}J$.

(1-x)	K, см$^{-1}$
0.3	7.1
0.4	12.2
0.7	15.7

In the region of ν~400 cm^{-1}, the antiresonance absorption (the Fano's effect) manifests itself clearly. In Fig.3 the corresponding feature is referred to as F.

The antiresonance becomes more pronounced with the increasing of the content of thallium component. It can be explained by increasing the role of the background non-structured absorption originated from the increase of the free charge (hole) concentration. Interaction of this absorption, meant in the frame of the Fano's concept [4], with the phonon resonance near 400 cm^{-1} manifests itself as a specific "falling in" on the absorption curve. Such effects (Fano's antiresonances), though less pronounced, are characteristic for some other frequencies.

The correlation dependences of *M(x)* and *F(x)* observed here, stimulated subsequently by studies on the $In_xTl_{1-x}J$ system, in particular, the measurements of polarized spectra at low temperatures, determination of antiresonance parameters [4], experiments using irradiation in the region of $h\nu > E_g$, determination of m_h^*, etc. However, out of some of the principal conclusions one can be made already on the base of results presented above.

Mechanism of structural transformations

The dependence of the structure of the IR absorption spectra on the changes of the component content and that is found by the authors in $In_xTl_{1-x}J$ solid solutions may be explained in terms of a specific phase transition. Under the conditions of small content of the thallium component, we deal with a typical solid substitution solution having a smooth (almost linear) dependence of the lattice parameters on x [1]. A subsequent increase of the Tl content imposes qualitative changes in the manner how

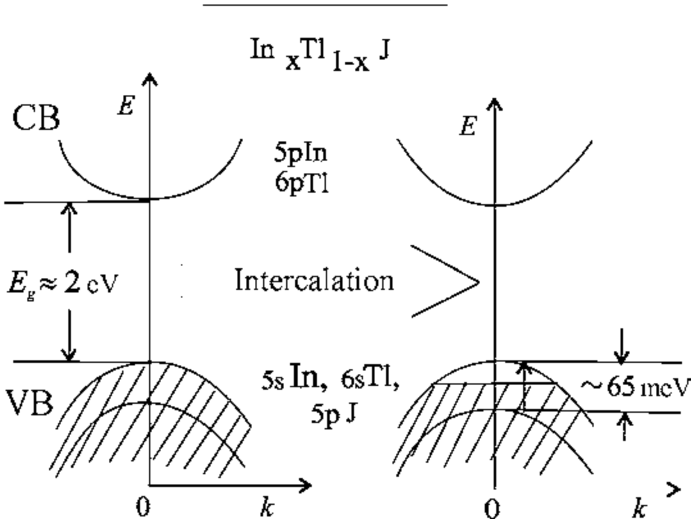

Fig.4. Inter-subband transitions in the $In_xTl_{1-x}J$ system.

the Tl^+ ions penetrate into the $In_xTl_{1-x}J$ lattice. Since the ionic radius of Tl^+ is larger than that of In^+ (r_{In+}=1.30Å, r_{Tl+}=1.49Å), an abrupt change in the solid solubility understood in a common sense, occurs when the ions are substituted in the sandwich layers. It is well known that the dimension factor is crucial for the realization of homogeneous solid solubility in the case of isovalence substitution. Restrictions for the solid solubility within a layer is caused, first of all, by the energy of elastic deformation of solid solution [6], $W(x)=\Omega_0\mu\beta^2 f(x)$ where Ω_0 is the ionic volume of the component being substituted (In^+), μ the displacement modulus, $f(x)$ being the geometric form-factor of the layer dependent on the component content, and

$$\beta= \frac{\Omega_{Tl^+}-\Omega_{In^+}}{\Omega_{In^+}}.$$

Qualitative changes of the location of Tl in the $In_xTl_{1-x}J$ lattice take place with increasing the content of the ions: some fraction of thallium ions substitute indium inside the layers, while the other fraction penetrates into the inter-layer space, thus promoting "metalization" of chemical bonds. Such the distribution is allowable owing to a layered structure of the lattice in the case of **b**>**a**,**c**.

Studies of the concentration dependences of the lattice parameters have shown that the factor of modification of the elementary cell, $\eta=(\mathbf{c}-\mathbf{a})/\mathbf{b})$ increases gradually with the increase of the Tl content [1]. However, this increasing is not monotonical: a break out is observed in the $\eta(x)$ dependence at $(1-x)\cong0.35$, whereas additional reflexes appear in the corresponding cristallograms [7]. The change in the slope of $\eta(x)$ at x≤0.65 is related to decreasing (**c-a**) and increasing the lattice parameter **a** (Table 2).

Table 2.Factor of modification of the $In_xTl_{1-x}J$ lattice.

x	$\eta,\times10^2$
0.3	2.20
0.5	3.06
0.6	3.52
0.7	3.96
0.8	4.09

We believe that the content of thallium component, at which the mentioned changes occur, corresponds to the limit of continuous intra-layer solubility of the $In_xTl_{1-x}J$ system. We have a case of a specific phase transition which does not change the lattice symmetry, the latter remaining orthorhombic. We choose to refer such a transformation to isostructural phase transition. The corresponding phases are designated as R1 and R2. As said above, the formation of the phase R2 is accompanied by a complex re-distribution of the thallium component. In particular, a process of auto-intercalation of the layered lattice comes to existence. A continuous transition from R1 to R2 testifies that we deal with a second-order phase transition.

The region in which the R1 and R2 phases coexist, due to a specific re-distribution of the thallium, is not only of interest as a manifestation of intercalation, but may have a practical meaning. Indeed, both the coordination and the charge state of thallium are different in the substituted positions within the layers, on the one side, and the positions inside the inter-layer gaps on the other. This enables one to control the free charge concentration.

Intermediate isostructural phase in the $In_xTl_{1-x}J$ system and the role of configuration interactions

The isostructural phase found for the first time in this study represents an intermediate phase of which the region of existence is determined both by the geometric isomorphism factor and the peculiarities of the structure of zone spectra characteristic for the components. The experimental and theoretical studies show that InJ is an indirect-zone material [6], contrary to TlJ which represents a direct-zone one [7]. This causes a notable difference in the normalized occupation density functions:

$$N^{d.}_{v,c}(\mathrm{E})=\frac{1}{(2\pi)^3}\int\delta[E_c(\vec{k})-E_v(\vec{k})]d\tau_{\vec{k}} \qquad (1)$$

$$N^{ud}_{v,c}(E)=\frac{1}{(2\pi)^6}\int\delta[E_c(\vec{k})-E_v(\vec{k}')]d\tau_{\vec{k}}d\tau_{\vec{k}'} \qquad (2)$$

Taking into account the properties of δ-function at $E \geq E_g$, one gets

$$N^{st.}_{v,c}(E)=\frac{[2\mu^3(h\nu-E_g)]^{1/2}}{2\pi^2h^3} \qquad (3)$$

$$N^{st.}_{v,c}(E)\sim g(h\nu-E_g)^2 ctg\frac{E_f}{2kT} \qquad (4)$$

where E_f denotes the actual phonon energy, and g the parameter of electron-phonon interaction.

As can be seen, the $N_{v,c}(E)$ functions for the InJ and TlJ components differ in the energy region of $E\sim E_g$ by the width and the height of peaks, as well as by the type of the Van Hove's singularities. This factor is associated with the features of iso-energy surfaces and the normalized occupation density function $N_{v,c}(E)$. According to generalized concept by Hume-Rothery, the given factor restricts the limits of solid solubility.

In the $In_xTl_{1-x}J$ system under study, a lower conduction band formed mainly by the p-states of cations is the most sensitive to the changes in content. The "drift" of the conduction band minimum in $In_xTl_{1-x}J$ from the k-k_{min} value for InJ (x=1) to the k=0 value for TlJ (x=0) reforms a topology of iso-energy surfaces in such a way that a break off in the solid solubility of the type of substitution inside the sandwich In-J-In layers happens at $x=x_k$. When $x<x_k$, a penetration of thallium into the inter-layer gaps (auto–intercalation) becomes possible, along with a process of chaotic formation of both simple and aggregated cluster centres. Statistical distribution of the clusters and possible interactions among them makes the situation more complicated. It is evident that the only possible way of their identification may be a method based on accounting for the features of the appropriate quantum states and the details of significance in the structure of the optical spectra. In this respect, the phonon and low-temperature exciton spectra are most sensitive [10].

The aggregation of cluster formations and, moreover, the auto-intercalation lead to nucleation of holes.

Keeping in mind a notable role of the band carriers, we qualify a rising of intermediate redistribution state as something like the phase transformation imposed by configuration interactions and hybridization of states.

From this point of view, it would be interesting to undertake the calculations of the redistribution charge density functions $\rho(\mathbf{r})$ for the cases of $In_xTl_{1-x}J$ solid solutions of different contents and to keep up with, e.g., the ρ changes in among In-In, In-Tl and Tl-Tl, while using statistically modeled problem *).

In this paper we suggest a somewhat indi-

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*) According to the calculation data for the $\rho(\mathbf{r})$ function, an increasing of electronic charge density located between the cations is observed within the orthorhombic structure. This demonstrates an essential role of configuration interactions among the cation orbitals and their hybridization.

rect approach that consists of assuming that the deviation of $E_g(x)$ dependence from the Vegard's law is a level of the configuration interaction:

$$E_g(x)=E_g(0)+[E_g(1)-E_g(0)]x-Ax(1-x) \qquad (5)$$

Using the methods of pseudo potential theory [11] and the specific modeling pseudo potential suggested by Heine-Abarenkov within the dielectric model by Phillips-Van Vechten [10], we have modified the expression for the A parameter with taking into account the Lorentzian crystal field correction η_L to the following form,

$$A=7.2\frac{\bar{e}_s^*}{e}\bar{\bar{\eta}}_L(r_A+\bar{\bar{r}}_K)\left(\frac{r_A-\bar{r}_K}{r_A\bar{r}_K}\right)^2 e^{-\frac{1}{2}\overline{kd}} \qquad (6)$$

where r_A and r_K denote, respectively, the anion and cation radii in, k the Thomas-Fermi quasi momentum in, d the inter-ion distance, and the averaged values of the lattice parameters for the $In_xTl_{1-x}J$ system are defined by the formula $\bar{a}=xa_{InJ}+(1-x)a_{TlJ}$.

In order to determine the effective Szigeti's charge we have made use of the relation

$$\frac{e_s^*}{e}=\frac{3\sqrt{\varepsilon_\infty}}{(\varepsilon_\infty+2)}\sqrt{\frac{\mu}{4\pi N}(\omega_{LO}^2-\omega_{TO}^2)} \qquad (7)$$

where $\mu=\frac{M_AM_K}{M_A+M_K}$ and N=z/V . The Lorentzian effective field correction is equal to $\eta=\frac{\varepsilon_\infty+2}{3}$ while the Thomas-Fermi number may be introduced according to Phillips empirical relationship [13],

$$k\cong 2.73\left[\frac{(Z_A+Z_K)_z}{V}\right]^{\frac{1}{6}} \qquad (8)$$

where Z_A and Z_K are the numbers of valence electrons related to the cation and the anion, respectively, z the number of formula units in the elementary cells, V the elementary cell volume. In our case $Z_j=7(5s^25p^5)$, $Z_{In}=3(5s^25p^1)$, $Z_{Tl}=3(6s^26p^1)$, z=4, $V_{InJ}=297.6Å^3$, $V_{TlJ}=309.4Å^3$.

The following parameters are obtained for the $In_{0.7}Tl_{0.3}J$ solid solution:

$\bar{k}$=1.95 Å, $\bar{d}$=3.42Å, $e^{-\frac{1}{2}\overline{kd}}$=3.556·$10^{-2}$, $\bar{r}_k$=1.357 Å, $\bar{\eta}_L$=3.092, $\bar{e}_s^*/e$=0.755, A=0.17eV.

The experimental $E_g(x)$ dependence for the InTlJ system is represented in [7].

With the aid of the relations $f_i=\frac{\varepsilon_\infty+2}{3\sqrt{\varepsilon_\infty}}\frac{\bar{e}_s^*}{e}$ and $\frac{g}{e}=\frac{2}{e_\infty}+0.6(1-f_i)$ we obtain the degree of bond ionicity f_i=0.865 and the charge value per bond g/e=0.356.

Conclusions

1. By using the IR spectroscopy technique, the isostructural phase transition and the intercalation phenomenon are revealed in the InTlJ system that appear under the conditions of changing the content of the solid solution. The mechanism of the appearance of the intermediate phase at the phase transformations is explained.

2. The essential role of free charges in formation of the structure of IR absorption spectra is shown.

3. Based on the pseudo potential theory and the dispersion model by Phillips-Van Vechten a number of parameters for the solid solution is determined.

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