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EFFECT OF DEFECTS OF A STRUCTURE ON PHASE TRANSITION TEMPERATURE

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Phenomenological ideas of changes in a phase transition temperature due to the defectiveness of structures in solids are developed, and their quantitative description is proposed. It is shown that a decrease in the phase transition temperature owing to the deterioration of the structural perfection of complex solids is proportional to the value of nonthermal spreading of Landau quantum levels, which is described by the Dingle temperature. The latter can be calculated theoretically and obtained from the experiments involving quantum oscillations.

Randomly fluctuating potential (RFP) arises due to structural defects including the nonuniform distribution of components of an alloy or a chemical compound. In semiconductors, RFP induces the nonthermal spreading of zone's edges, which is equivalent to a nonthermal spreading of quantum levels by $\Delta E \approx \epsilon_0^{-1}(Nr)^{1/2}$ (ϵ_0 is the permittivity, N is the defect concentration, and r is the action radius of a disturbing potential). The latter allows one to experimentally estimate the value of ΔE by the nonthermal spreading of quantum levels which is described by the Dingle temperature $T_{\rm D}$ ($\Delta E = kT_{\rm D}$) [1]. In the experiments involving quantum oscillations, $T_{\rm D}$ defines the damping of the amplitude of oscillations and is the defectiveness measure of crystals at $T = 0$ K. Then the order parameter Q can be written in the general case as

$$Q = \gamma(D - T)^{\beta}, \quad D = T_{\rm D} + T_c, \tag{1}$$

where γ is a coefficient, D is the phase transition temperature of an ideal monocrystal, T_c is the temperature of a real phase transition, and β is the critical index of the order parameter. In this case, it is assumed that a decrease in the phase transition temperature with increase in the crystal lattice defectiveness can be described by the Dingle temperature. In complex semiconductors and metals, $T_{\rm D}$ reaches, respectively, 53 K and is at most 1 K [2].

Structural phase transitions in solid solutions $A^{IV}B^{VI}$ were the object of numerous studies [3—11]. As known, the instability of a crystal lattice is typical of narrow-gap semiconductors $Pb_{1-x}Sn_xTe$ in the interval of compositions $0.2 \leq x \leq 1.0$ and temperatures $4.2 < T < 300$ K, which leads to a ferroelectric structural phase transition of the II kind (of the shear type) from the cubic (O_h) to rhombohedral (C_{3v}) phase under a lowering of temperature. In [5], the existence of three phase transitions was revealed by X-ray structure analysis in powders, two of them being characterized by changing a crystal lattice symmetry [5].

Free current carriers and the structural defects of a crystal lattice influence phase transitions. It was shown earlier [6, 7] that the temperature dependences of thermoelectromotive force (TEMF) and magnetic susceptibility (MS) bear a useful information for studying the phase transitions in $A^{IV}B^{VI}$. This is related to the influence of structural phase transitions on the forbidden gap width E_g, which is essential in connection with its small value in narrow-gap semiconductors. In the present work, we present the results of complex investigations of the neutron diffraction, TEMF α, MS χ, specific resistance in the temperature interval 4.2—300 K, and Shubnikov's oscillations of TEMF in magnetic fields up to 4 T. We studied monocrystals of $Pb_{1-x}Sn_xTe$ ($x = 0.2$) with high structural perfection which were grown from the vapour phase with the concentration of current carriers $p = 2 \cdot 10^{-17}$ cm^{-3}. By the data on one-frequency oscillations of TEMF in these specimens, $T_{\rm D} = (8 \pm 1.2)$ K.

Neutron diffraction studies were implemented on a nuclear impulse fast-fission reactor ИБР-2 at the Joint Institute of Nuclear Research (Dubna) with the use of a diffractometer ДН-2 by time-of-flight neutron diffractometry. Fig. 1 shows the example of a neutron diffraction spectrum in the direction [111] which was derived at 290 K. In the energy range under study, we observed two peaks from the planes {222} and {111}. Similar spectra were obtained in the temperature range 20—290 K with a step of 10 K.

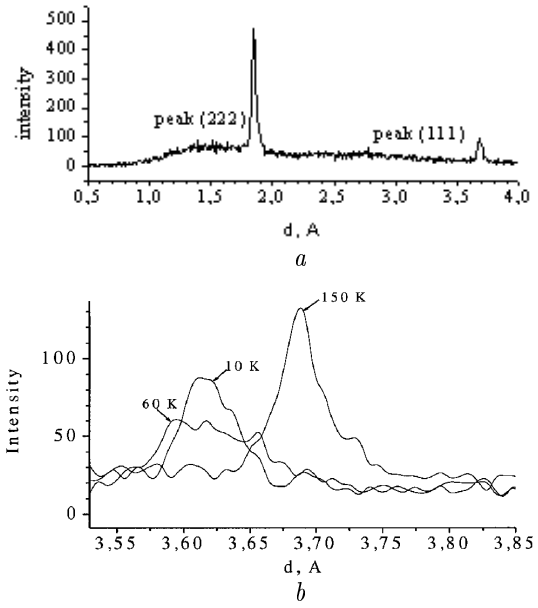

Fig. 1. a — neutron diffraction spectrum for the direction [111] at $T = 290$ K; diffraction peaks are observed for planes {111} and {222} ; b — diffraction maxima (111) for typical temperature regions

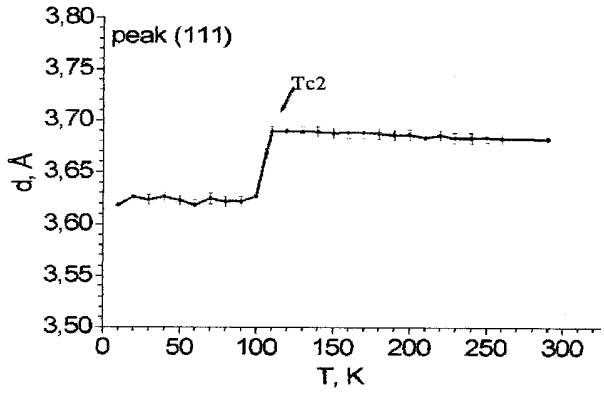

Fig. 2. Interplanar distance d for peak (111) vs temperature. The arrow indicates the phase transition at $T_{c2} = (110 \pm 5)$ K

In Fig. 1,b, we present the temperature changes of the position of the peak (111) for typical temperature regions. We emphasize the decreasing and splitting of the peak at $T = 60$ K.

Fig. 2 demonstrates the temperature dependence of the interplanar distance in the direction [111]. Its sharp change at (110 ± 5) K which is more than 1% indicates the drastic change in the lattice period in this temperature region, which can be caused by a phase transition.

A change in interplanar distances is associated with that in interatomic bindings, which leads to a change

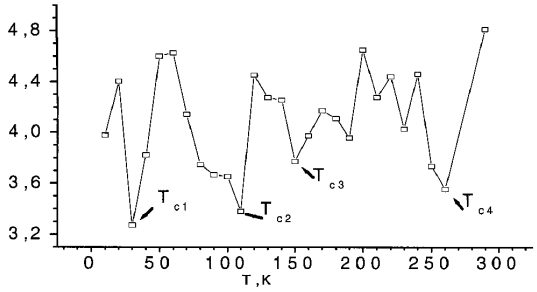

Fig. 3. Temperature dependence of the ratio of the intensities of peaks (111)/(222). $T_{c1} = (35 \pm 5)$, $T_{c2} = (110 \pm 5)$, $T_{c3} = (140 \pm 5)$, and $T_{c4} = (260 \pm 5)$ are the temperature of phase transitions

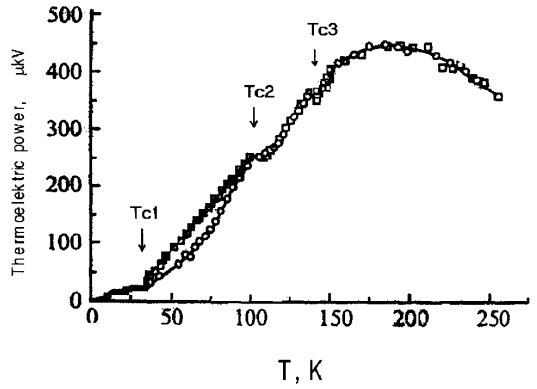

Fig. 4. Temperature dependence of TEMF [6]. The designations are the same as in Fig. 3. Studies were carried out under cyclic cooling and heating of the specimen. The hysteresis of TEMF was observed in the region $T_{c1} \leq T \leq T_{c2}$

in the peak intensities of the diffraction spectra under phase transitions. On this foundation, the minima on the temperature dependences of the ratio of the reflection peak intensity from plane {111} to that from plane {222} (see Fig. 3) indicate the phase transitions at $T_{c1} = (35 \pm 5)$ K, $T_{c2} = (110 \pm 5)$ K, $T_{c3} = (140 \pm 5)$ K, and $T_{c4} = (260 \pm 5)$ K.

The comparison of these results with the data on the temperature dependences of TEMF (Fig. 4) and MS (Fig. 5) and with the results of X-ray structure analysis [5] confirms the presence of four successive phase transitions in $Pb_{1-x}Sn_xTe$ ($x = 2$).

In the temperature interval $T_{c1} < T < T_{c2}$, TEMF reveals a low-area hysteresis loop, which testifies to a phase transition of the I kind. The hysteresis is related to both the creation of nuclei of other phase and the energy expense for the increase in their surface. To the best of our knowledge, a hysteresis loop of TEMF under a phase transition of the shear kind was observed for the first time. At $T \approx T_{c3}$, we see the weak anomaly of

a monotone behaviour of the temperature dependence of TEMF.

A particular attention should be paid to the fact that the top of reflex (111) is split in the hysteresis region in the range $T = 90 \div 40$, its intensity being minimum at $T \approx 60$ K. The further decrease in temperature causes the increase in the intensity and the disappearance of the splitting.

The temperature dependence of MS $\chi(T)$ has two peculiarities revealed as the increase in paramagnetism against the diamagnetic background near temperatures T_{c1} and T_{c3}. Indeed, the phase transitions are accompanied by the appearance of an addition to the forbidden gap width E_g which depends on temperature. In connection with the smallness of E_g in narrow-gap semiconductor $Pb_{0.8}Sn_{0.2}Te$, the renormalization of the zone spectrum must induce a change in its magnetic and kinetic properties. Moreover, the addition to MS arises, which is caused by fluctuations of the order parameter in the region of phase transitions [11]. The latter yields, possibly, weakly pronounced changes in $\chi(T)$ near T_{c2}.

Thus, increasing the structural perfection of monocrystals of the solid solutions of $Pb_{0.8}Sn_{0.2}Te$ have led to increasing the temperature of the lowest-temperature phase transition from (19—26) K to $T_{c1} = (35 \pm 5)$ K, the appearance of other phase transition at $T_{c2} = (110 \pm 5)$, and the hysteresis of TEMF in the temperature range between the first and second phase transitions.

The concentration of current carriers N in the solid solutions of $Pb_{1-x}Sn_xTe$ is defined by the vacancies of a metal or chalcogene. In turn, this defines the minimally possible concentration of the packing defects of a monocrystal. According to [1], one can calculate the value of T_D for any composition of the solid solution for a given concentration of current carriers as

$$T_D \approx e^2(k\epsilon_0^*)^{-1}(\pi r N)^{1/2}, \quad r = (6e^2N/\epsilon_0 E_F)^{-1/2} \qquad (2)$$

where ϵ_0^* is the effective value of MS in the region of a structural defect [1] and E_F is the Fermi energy. Since $E_F \sim N^{2/3}$, $r \sim (E_F/N)^{1/2} \sim N^{-1/6}$, we get in the general case:

$$T_D \sim N^{0,416}. \qquad (3)$$

The comparison of our experimental data with the results of calculations by (2) demonstrates a good agreement (see Fig. 6). For the specimen under study, the calculation by (2) yields $T_D = 8.3$ K, which well correlates with the experimental value $T_D = (8 + 1.2)$ K. This fact testifies to a high quality of the monocrystal and allows us to estimate D.

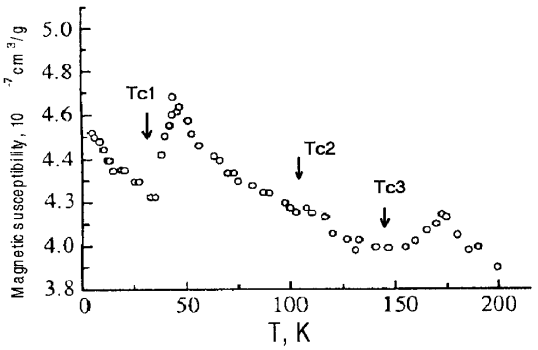

Fig. 5. Temperature dependence of permeability [6]. The designations are the same as in Fig. 3

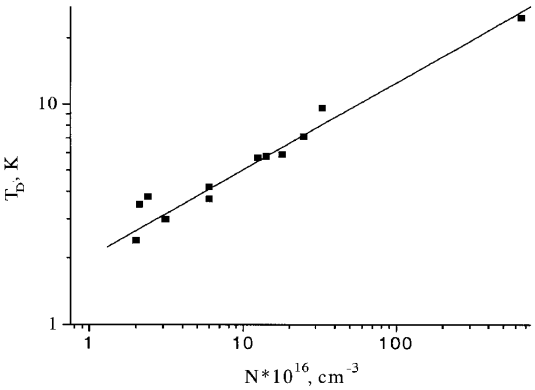

Fig. 6. Dependence of the Dingle temperature on the concentration of current carriers in the solid solution of $Pb_{1-x}Sn_xTe$ ($x = 2$) (the continuous line is a result of calculations, and the points present experimental data)

By (1), we get $D_1 = (43 \pm 6)$ K and $D_2 = (118 \pm 6)$ K. By X-ray structure analysis, the authors of [5] observed the structural instability of the lattice period in a crushed monocrystal of $Pb_{1-x}Sn_xTe$ ($x = 0.2$) in the range 10—80 K. It is possible to assume that the reasons for this instability are the same as those which induce the hysteresis of TEMF and the splitting of diffraction maxima in the range $T_{c1} - T_{c2}$. In addition, for both specimens, $\Delta T_c = T_{c2} - T_{c1}$ are the same to within the experimental error.

This allows us to determine $T_D = (33 \pm 5)$ K from the temperature of the first phase transition for a powder. Substituting this value of T_D to (2), we get $D_2 = (113 \pm 10)$ K. Thus, the values of D_2 estimated in independent experiments with two specimens of $Pb_{1-x}Sn_xTe$ ($x = 0.2$) with sharply different levels of structural perfection are, in fact, identical, the difference being less than 5%.

Thus, the phase transition temperature decreases with increase in the crystal lattice defectiveness by

a value which is at least T_D. Moreover, the Dingle temperature can be considered the measure of structural perfection of solids.

In the temperature interval $(T_{c1} - T_{c2})$ where the hysteresis of TEMF is observed, we found the splitting of reflection peaks in the neutron diffraction spectrum, which indicates both the I kind of the phase transition and the reduction of a crystal lattice symmetry.

The joint analysis of the results of neutron diffraction, thermoelectric and magnetic studies has demonstrated the existence of four phase transitions at (35 ± 5), (110 ± 5), (140 ± 5), and (260 ± 5) K. In the last case, it is necessary to carry out additional studies of thermoelectric and magnetic properties.

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ВПЛИВ ДЕФЕКТІВ СТРУКТУРИ НА ТЕМПЕРАТУРУ ФАЗОВОГО ПЕРЕХОДУ

О.І. Дмитрієв

Р е з ю м е

Розроблено феноменологічні уявлення та запропоновано кількісний опис зміни температури фазових перетворень внаслідок дефектності структури у твердих тілах. Показано, що зниження температури фазових перетворень внаслідок погіршення структурної досконалості складних твердих тіл, пропорційно величині нетеплового розширення квантових рівнів Ландау, що описується температурою Дінгла. Останнє може бути розраховано теоретично, а також одержано з квантових осциляційних експериментів.

ВЛИЯНИЕ ДЕФЕКТОВ СТРУКТУРЫ НА ТЕМПЕРАТУРУ ФАЗОВОГО ПЕРЕХОДА

А.И. Дмитриев

Р е з ю м е

Разработано феноменологическое представление и предложено количественное описание понижения температуры фазовых превращений вследствие возрастания дефектности структуры в твердых телах. Показано, что такое понижение пропорционально величине нетеплового расширения квантовых уровней Ландау, что описывается температурой Дингла. Последнее может быть рассчитано теоретически, а также измерено экспериментально по данным квантовых осцилляционных эффектов.