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Galvanomagnetic properties and electronic structure of iron-doped PbTe

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	10	We synthesize an iron-doped PbTe single-crystal ingot and investigate the phase composition and
	11	distribution of the iron impurity along the ingot as well as galvanomagnetic properties in weak
	12	magnetic fields (4.2 K $\leq T \leq$ 300 K, B \leq 0.07 T) of Pb _{1-v} Fe _v Te alloys. We find microscopic inclu-
	13	sions enriched with iron and regions with a chemical composition close to FeTe in the heavily
	14	doped samples, while the iron impurity content in the main phase rises only slightly along the
	15	length of the ingot reaching the impurity solubility limit at approximately 0.6 mol. %. Samples
	16	from the initial and the middle parts of the ingot are characterized by <i>p</i> -type metal conductivity. An
	17	increase of the iron impurity content leads to a decrease in the free hole concentration and to a sta-
	18	bilization of galvanomagnetic parameters due to the pinning of the Fermi level by the iron resonant
	19	impurity level $E_{\rm Fe}$ lying under the bottom of the valence band ($E_{\rm v} - E_{\rm Fe} \approx 16 {\rm meV}$). In the samples
	20	from the end of the ingot, a <i>p</i> - <i>n</i> inversion of the conductivity type and an increase of the free elec-
	21	tron concentration along the ingot are revealed despite the impurity solubility limit being reached.
	22	The kinetics of changes of charge carrier concentration and of the Fermi energy along the ingot is
	23	analyzed in the framework of the six-band Dimmock dispersion relation. A model is proposed for
	24	the electronic structure rearrangement of $Pb_{1-y}Fe_yTe$ with doping, which may also be used for
	25	PbTe doped with other transition metals. © 2015 AIP Publishing LLC.
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I. INTRODUCTION 26

It is well known that PbTe-based alloys are among the 27 28 most efficient thermoelectric materials for mid-range temperature (500–900 K) applications.^{1–3} However, the maxi-29 mum value of their thermoelectric figures of merit 30 $ZT = \sigma S^2 T / \kappa$ (σ —electrical conductivity, S—Seebeck coeffi-31 cient, T—absolute temperature, and κ —thermal conductiv-32 ity) did not exceed 1.0 for a long time. In recent years, there 33 has been a revival of interest in the PbTe-based alloys as 34 effective thermoelectric materials.^{2–6} One of the reasons for 35 this is the discovery of a substantial increase of the ZT value 36 37 when these semiconductors are doped with group III,^{7,8} rareearth,^{9,10} or transition metal^{11,12} impurities. Such impurities 38 introduce resonant impurity levels inside the conduction or 39 valence bands, resulting in an increase of the Seebeck coeffi-40 41 cient S due to a distortion and a sharp increase of the density of states near the Fermi level located in the vicinity of the 42 resonant impurity-induced level.¹³ 43

Among all currently known impurity levels of transition 44 metals in PbTe the most studied is the resonant level of 45 46 Cr, located approximately 100 meV above the bottom of the conduction band at T = 4.2 K.^{14–16} Resonant levels of two 47 light transition metal impurities (Ti, Sc) are even deeper in 48 the conduction band (200-230 meV (Refs. 17-19) and 49 approximately 280 meV (Ref. 20) above the bottom of the 50

conduction band, respectively), whereas the V level is the 51 only deep level in the band gap (approximately 20 meV 52 (Refs. 21–23) under the bottom of the conduction band). All 53 of these impurities act as donors inducing a *p*-*n* inversion of 54 the conductivity type in an initially undoped PbTe. However, 55 fabrication of a thermoelectric device requires materials of 56 both *n*- and *p*-types, i.e., materials with resonant impurity 57 levels inside the conduction and valence bands, respectively. 58

Recently, we have found that Fe-induced impurity level 59 in PbTe is the first and still the only known transition metal 60 impurity level located in the valence band (15-20 meV 61 below the top of the valence band at T = 4.2 K).²⁴ It was 62 shown that doping of initially undoped *p*-type crystals leads 63 to a decrease of the free hole concentration and to the pin-64 ning of the Fermi level by the resonant Fe level. Subsequent 65 doping is not expected to affect the galvanomagnetic proper-66 ties and the concentration of free holes. This effect, associ-67 ated with the pinning of the Fermi level, was indeed 68 observed in a limited range of the impurity content, but a p-n69 inversion of the conductivity type and an increase in the con-70 centration of free electrons was unexpectedly found at higher 71 impurity concentrations. 72

In this paper, we present results of detailed studies of 73 elemental and phase compositions of an iron-doped PbTe 74 single-crystal ingot and the galvanomagnetic properties of 75 $Pb_{1-v}Fe_{v}Te$ alloys in weak magnetic fields $(4.2 \text{ K} \le T)$ \leq 300 K, **B** \leq 0.07 T) in the vicinity of the *p*-*n* conversion 77 point. The main goals are to investigate the kinetics of 78

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⁷⁹ changes in the free charge carrier concentration with doping, to elucidate the reasons for the breakdown of the Fermi level pinning in heavily doped alloys, and to construct a model of the electronic structure rearrangement in $Pb_{1-y}Fe_yTe$ upon doping.

84 II. EXPERIMENTAL DETAILS

A single crystal $Pb_{1-v}Fe_vTe$ ingot with nominal Fe con-85 tent y = 0.02 was grown using the vertical Bridgman tech-86 nique from a mixture of pre-synthesized PbTe and FeTe₂ by 87 reacting the pure elemental constituents (Pb-99.9999%, 88 Fe—99.999%, Te—99.9999% after additional zone-refining 89 and double vacuum distillation). Pb was subjected to addi-90 tional chemical cleaning to remove surface oxides before 91 loading into the synthesis or growth ampoule. For this pur-92 93 pose, etching in a water solution of nitric acid $(1HNO_3 + 3H_2O)$ heated to 90 °C was used. After etching, 94 Pb was washed with a large amount of distilled water, and 95 then with chemically pure acetone, in several glass 96 97 containers.

High-purity carbonyl iron was used for the synthesis of 98 iron ditelluride at 950 °C for 96 h. The choice of FeTe₂ as 99 dopant is justified by its lower melting point in comparison 100 to Fe or FeTe, enabling the most efficient mixing of the melt 101 components in the growth ampoule placed on the tempera-102 ture plateau at 980 °C. Excessive Te from the FeTe₂ was bal-103 104 anced with an equal molar amount of Pb to obtain stoichiometric $Pb_{1-v}Fe_vTe$. 105

Synthesis of PbTe and FeTe₂ as well as the growth of 106 the single crystal $Pb_{1-v}Fe_{v}Te$ were carried out in quartz 107 ampoules evacuated to 10^{-5} Torr. Their inner surface was 108 coated with pyrolytic graphite in order to minimize the con-109 tact of melt with quartz and to avoid sticking of the cooled 110 ingots. Graphite coating technique was as follows. First, 111 quartz ampoules were deeply cleaned by etching in a mixture 112 113 of acids $(7HF + 3HNO_3)$ followed by washing with distilled water, steaming and hot drying. Then they were heated to 114 1100 °C for 1-2 h under continuous evacuation. Afterwards 115 the temperature was lowered to 900 °C and the ampoule was 116 connected to a vapor source of chemically pure acetone. 117 Pyrolysis was carried out within 15 minutes at a pressure of 118 0.2 atm. Then the ampoule was evacuated to 10^{-3} Torr, 119 heated to 1100 °C, and kept at this temperature for 120 30-40 min. As a result, the inner surface of the quartz am-121 poule was covered with a solid graphite film. 122

123 During the crystal growth, the temperature gradient at the solid-liquid interface reached 35°C/cm, whereas the 124 growth rate was 1 mm/h. The growth axis of the single crys-125 tal $Pb_{1-y}Fe_yTe$ coincided approximately with the $\langle 111 \rangle$ 126 127 crystallographic direction. The resulting ingot weighing 33 g was cut perpendicular to the growth axis into 26 disks of 128 approximately 10.5 mm in diameter, each about 1.5 mm 129 thick, via wire cutting using a tungsten 0.25 mm wire. An 130 131 equal volume part mixture of glycerol and Al₂O₃ powder with a maximum grain size of 30 μ m was used for the cut-132 133 ting. The vertical cutting speed was 0.5 mm/min.

The integral concentration of iron *y* was determined on both sides of each disk, in the central part of diameter 5 mm, J. Appl. Phys. **118**, 000000 (2015)

using an X-ray fluorescence spectrometer TRACOR 5000 136 XRF (USA). The obtained values were averaged and satis- 137 factorily fitted by the sum of a constant and two exponential 138 terms^{25,26} (Fig. 1) 139

$$y = y_0 + A_1 e^{-L/t_1} + A_2 e^{L/t_2},$$
 (2.1)

where *L* is the relative longitudinal coordinate ranging from 1400 to 1; y_0, A_1, A_2, t_1, t_2 are dimensionless fitting parameters. 141

In addition, the phase composition and the homogeneity 142 of the disks as well as the distribution of Fe impurity along 143 the ingot axis in the main phase were determined by X-ray 144 fluorescence microanalysis using the scanning electron 145 microscope LEO SUPRA 50VP (Germany) with the INCA 146 Energy microanalysis system (Oxford Instruments, 147 England). Data on the iron content obtained by the two methods are in satisfactory agreement in the interval 0.4 < L < 0.9 149 (see Fig. 1).

To study the galvanomagnetic effects, samples in the 151 form of rectangular parallelepipeds with typical dimensions 152 of $4.0 \times 0.7 \times 0.7$ mm³ were cut from the disks using an electric discharge machine. All samples were etched in a solution 154 of bromine in hydrobromic acid and carefully washed in 155 ethyl alcohol and distilled water. Electrical contacts to 156 the samples were fabricated from In-coated Cu wires 157 0.03–0.05 mm in diameter. Current contacts were soldered 158 by a micro soldering iron to the ends of the samples using an 159 In + 4%Ag + 1%Au alloy. Potential and Hall contacts were 160 electrowelded to the samples using an electric-spark setup. 161 Four-probe dc method was used to investigate the tempera- 162 ture dependences of the resistivity ρ , of the Hall coefficient 163 R_H , and of the Hall mobility μ_H in weak magnetic fields 164 $(4.2 \text{ K} \le T \le 300 \text{ K}, \mathbf{B} \le 0.07 \text{ T}).$ 165



FIG. 1. Distribution of iron along the $Pb_{1-y}Fe_yTe$ ingot obtained by the XRF integral method (open squares) for both the main and secondary phases, and by XRF microanalysis (black circles) for the main phase. The solid curve represents the approximation (2.1) of the iron distribution. In the inset, *h* is the distance from the beginning of the ingot to the middle of the disk, h_0 is the total length of the ingot, *R* and $L = h/h_0$ are the diameter and the relative coordinate of the disk, respectively.

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166 III. PHASE AND ELEMENTAL COMPOSITIONS OF THE167 SAMPLES

The phase and elemental compositions of the samples 168 were monitored on the surfaces of the initial disks cleaved in 169 liquid nitrogen. Figure 2 shows typical microphotographs of 170 such surfaces and the X-ray emission spectra from the indi-171 172 cated areas for samples from the middle part of the ingot (the numbers on the photographs correspond to the serial num-173 bers of disks). We find that practically all samples (samples 174 from the disks 20 to 4) contain clearly defined microscopic 175 176 inclusions of a secondary phase (dark areas in Figs. 2(a) and 2(b)) embedded inside a matrix of the main phase. These 177 inclusions are enriched with iron and their chemical compo-178 sition corresponds to alloys $Pb_{1-y}Fe_yTe$ with different (up to 179 50%) iron content in the metal sublattice. In samples from 180 the beginning and the end of the ingot (especially in the sam-181 ple from disk 2) regions with a chemical composition close 182 183 to FeTe are detected. Moreover, periodic spatial structures of alternating phases are observed in sample 2 (Fig. 3(a)). In 184 other words, at the very end of the ingot, which is strongly 185 enriched in iron, PbFeTe phase spontaneously form lamellae 186 of $Pb_{1-v}Fe_{v}Te$ with moderate (0.5%-1.0%) iron concentra-187 tion (light regions in Fig. 3(a)) and lamellae of FeTe (dark 188 regions in Fig. 3(a)). These results allow us to conclude that 189 the solubility limit of iron impurity is exceeded in almost all 190 investigated samples, which is obviously due to the high ini-191 tial iron content in our ingot. 192

We find that within the experimental error, the main phase in all investigated samples is fairly uniform. However, the spatial distribution of impurities along the length of the 195 ingot is different than the one expected based on the experi-196 mental data obtained previously for rare-earth and other tran-197 sition metal impurities in PbTe-based alloys^{25,26} and on the 198 data obtained by the integral X-ray fluorescence method (see 199 Fig. 1). The concentration of the iron impurity in the main 200 phase increases along the ingot by no more than 1.5 times, 201 reaching only 0.6 mol. %. In addition, the error in determin- 202 ing the concentration of impurity is comparable with or even 203 exceeds the concentration itself. Despite these observations, 204 as we will see below, galvanomagnetic parameters and the 205 concentration of free charge carriers vary along the ingot by 206 orders of magnitude, as if the Fe impurity concentration 207 monotonically and significantly increased when moving 208 from the beginning to the end of the ingot. 209

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IV. GALVANOMAGNETIC PROPERTIES

The investigation of temperature dependences of the re- 211 sistivity ρ , the Hall coefficient R_H , and the Hall mobility 212 $\mu_H = R_H/\rho$ shows that $Pb_{1-y}Fe_yTe$ samples from the initial 213 and middle parts of the ingot (samples 24 to 10) are charac- 214 terized by a *p*-type metal-like conductivity (Fig. 4). As the 215 temperature grows, the resistivity increases by up to three 216 orders of magnitude, while the Hall coefficient is positive in 217 the whole investigated temperature range. The Hall mobility 218 μ_H exhibits behaviors typical for undoped PbTe-based 219 alloys: a power law of mobility versus temperature (μ_H 220 $\propto T^{-\alpha}$, $\alpha \approx 2.1$) in a wide high temperature range due to the 221 scattering of holes on the acoustic phonons, and low- 222



FIG. 2. Scanning electron microscope photographs of cleaved surfaces (a) and (b) clearly showing microscopic inclusions of a secondary phase and the X-ray emission spectra (c) and (d) obtained from the selected areas of $Pb_{1-y}Fe_yTe$ samples. The numbers on the photographs correspond to the serial numbers of the disks into which the ingot was cut.

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FIG. 3. Scanning electron microscope photograph of a cleaved surface (a) showing embedding of regions of one composition inside a matrix of another composition and the X-ray emission spectra (b) and (c) obtained from the selected areas of $Pb_{1-y}Fe_yTe$ sample. The number on the photograph corresponds to the serial number of the disk.

temperature saturation of mobility at approximately 10^5 cm² V⁻¹ s⁻¹ due to the scattering of holes on charged point defects (mainly nonstoichiometric native defects).

At liquid-helium temperatures, dependences of ρ , R_H , 226 227 and μ_H versus the sample sequential number tend to a saturation. Moreover, in samples 16 to 10, temperature dependen-228 ces of galvanomagnetic parameters are almost identical (see 229 Fig. 4). In addition, the temperature dependences of the Hall 230 231 coefficient have an anomalous character in these samples: as the temperature rises, the Hall coefficient increases by more 232 than an order of magnitude, passes through a maximum at 233 T = 100-120 K, and then decreases to room temperature. A 234 235 similar behavior of the Hall coefficient was observed earlier in *n*-type PbTe-based alloys doped with In, Ga, and Cr with 236 resonant impurity levels inside the conduction band.^{15,27-29} 237 In all these cases, an increase of the absolute value of R_H 238 was successfully explained by the flow of electrons from the 239



FIG. 4. Temperature dependences of the resistivity ρ (a), the Hall coefficient R_H (b) and the Hall mobility μ_H (c) in p-Pb_{1-y}Fe_yTe. The numbers on the curves correspond to the serial numbers of the disks into which the ingot was cut.

conduction band to the resonant level due to the pinning of 240 the Fermi level by the resonant impurity level and an 241 increase of the band gap (i.e., a shift of the Fermi energy 242 downwards with respect to the bottom of conduction band) 243

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with temperature, while the decrease of R_H at high tempera-244 tures was associated with the increase of the free electron 245 246 and hole concentrations due to the intrinsic thermal ionization. Thus, by analogy with cases of In, Ga, and Cr impurity 247 levels in PbTe-based alloys, we can conclude that the anom-248 alous behavior of the Hall coefficient in Pb_{1-v}Fe_vTe alloys 249 also indicates the pinning of the Fermi level by the Fe impu-250 251 rity resonant level located under the bottom of the valence 252 band.

Based on this analogy, one may conjecture that due to 253 the pinning of the Fermi level, further doping should affect 254 neither the position of the Fermi level nor the concentration 255 256 of free charge carriers in the alloy. However, we observe an abrupt change of sign and a gradual decrease in the absolute 257 value of the Hall coefficient in samples 8 to 4 (Fig. 5), indi-258 cating a p-n conversion and an increase in the concentration 259 260 of free electrons in the conduction band. Only in sample 2, which has the maximum integral impurity concentration, 261 does this overall trend of changes in the galvanomagnetic pa-262 rameters along the ingot break down, likely due to a sharp 263 264 increase in the share of the secondary phase at the end of the ingot (see Fig. 5). Nevertheless, even in this sample we 265 observe a high value of Hall mobility ($\mu_H \approx 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) 266 that exhibits the spatial alternation of the main and second-267 ary phases. This implies the persistence of high structural 268 perfection of the main phase even in heavily doped samples. 269 Moreover, this fact suggests that the n-type $Pb_{1-v}Fe_{v}Te$ 270 alloys also have a potential for practical application associ-271 ated with a substantial excess of the solubility limit of the 272 impurity and spontaneous formation of periodic spatial struc-273 tures of alternating phases at the end of the ingot. In this 274 case, an increase of thermoelectric figure of merit ZT can be 275 276 achieved by reducing the phonon part of the thermal conductivity as a result of additional scattering of phonons on mi-277 croscopic inclusions enriched with iron and on the phase 278 boundaries in terms of preserving the existing high values of 279 mobility of charge carriers and therefore conductivity in 280 heavily doped crystals. 281

In all *n*-type samples, temperature dependences of the 282 resistivity ρ and of the Hall coefficient R_H have "metallic" 283 character typical for undoped PbTe-based alloys with no de-284 tectable peculiarities associated with the pinning of the 285 Fermi level (see Fig. 5). We observe high-temperature acti-286 vation sections in $\rho(T)$ and $R_H(T)$ only in samples 8 and 2, 287 288 which have the largest Hall coefficients (i.e., the smallest concentration of free electrons) at low temperatures. This is 289 obviously due to the intrinsic thermal ionization. These 290 experimental results indicate a breakdown of pinning of the 291 Fermi level in heavily doped $Pb_{1-v}Fe_vTe$ alloys, which is a 292 characteristic feature of almost all PbTe-based semiconduc-293 tors doped with variable valence impurities (group III metals, 294 rare-earth and transition metals). 295

296 V. KINETICS OF FREE CHARGE CARRIER 297 CONCENTRATION AND THE MODEL OF ELECTRONIC 298 STRUCTURE REARRANGEMENT WITH DOPING

To determine the position of the iron resonant level $E_{\rm Fe}$ with respect to the top of the valence band, to construct a



FIG. 5. Temperature dependences of the resistivity ρ (a), the Hall coefficient R_H (b) and the Hall mobility μ_H (c) in n-Pb_{1-y}Fe_yTe. The numbers on the curves correspond to the serial numbers of the disks into which the ingot was cut.

diagram of electronic structure rearrangement with doping in 301 $Pb_{1-y}Fe_yTe$ alloys, and to elucidate the reasons for the 302 breakdown of the Fermi level pinning, we plot the dependen-303 ces of free charge carrier concentration p(n) and the Fermi 304

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energy E_F at liquid-helium temperature versus the serial 305 number of the sample in the Pb_{1-v}Fe_vTe ingot. Assuming 306 307 degenerate statistics of holes and electrons in all investigated samples, we determine the free charge carrier concentration 308 from the absolute value of the Hall coefficient R_H as 309 $p(n) = 1/e|R_H|$, where *e* is the elementary charge (Fig. 6(a)). 310 Then, we calculate the position of the Fermi level with 311 respect to either the top of the valence band or the bottom of 312 the conduction band (Fig. 6(b)) from the experimental values 313 of the free charge carrier concentration using the nonpara-314 bolic six-band Dimmock dispersion relation for IV-VI 315 semiconductors^{30,31} 316

$$\begin{pmatrix} \frac{E_g}{2} + \frac{p_{\perp}^2}{2m_l^-} + \frac{p_{||}^2}{2m_l^-} - E \end{pmatrix} \left(-\frac{E_g}{2} - \frac{p_{\perp}^2}{2m_t^+} - \frac{p_{||}^2}{2m_l^+} - E \right)$$

$$= E_{\perp} \frac{p_{\perp}^2}{2m_0} + E_{||} \frac{p_{||}^2}{2m_0},$$

$$(3.1)$$

where E is the energy of electrons or holes measured from 317 the middle of the band gap, $E_g = 190 \text{ meV}$ is the direct band 318 gap of PbTe at the L points of the Brillouin zone, p_{\perp} and p_{\parallel} 319 are the transverse and longitudinal components of momen-320 tum, $E_{\perp} = 2P_{\perp}^2/m_0, E_{\parallel} = 2P_{\parallel}^2/m_0, P_{\perp}$, and P_{\parallel} are the ma-321 trix elements of transverse and longitudinal momenta 322 characterizing the interaction of the valence and conduction 323 bands, m_t^{\pm} and m_l^{\pm} are additional parameters taking into 324 325 account the interaction of the principal bands with the four distant bands in the second-order $\mathbf{k} \cdot \mathbf{p}$ method perturbation 326 theory, and m_0 is the free electron mass. 327

The calculation of the Fermi energy, described in detail 328 in Ref. 20, was performed using ellipsoidal truncation of the 329 six-band model³¹ and one for the most reliable set of model 330 parameters determined in Refs. 32 and 33. Figure 6 shows 331 that the free hole concentration rises along the ingot and 332 tends to saturate at $p_{sat} \approx 6 \times 10^{17} \text{ cm}^{-3}$ (samples 16 to 10). 333 The Fermi level shifts up and stabilizes by the Fe-induced 334 resonant level $E_{\rm Fe}$ below the top of the valence band ($E_{\rm v}$ 335 $-E_{\rm Fe} \approx 16 \,{\rm meV}$) for the same samples. Then a *p*-*n* inversion 336 337 of the conductivity type and an increase of the free electron 338 concentration take place. Only in sample 2, in which 339 regions with characteristic spatial alternation of the main



FIG. 6. Kinetics of changes of the free charge carrier concentrations (a) and of the Fermi level E_F relative to the edges of the bands (b) at the liquidhelium temperature along the Pb_{1-y}Fe_yTe ingot.

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 $(Pb_{1-y}Fe_yTe)$ and secondary (FeTe) phases were detected, 340 are the values of *n* and E_F significantly lower than in the previous samples 4 and 6. 342

In general, the kinetics of changes in the charge carrier 343 concentration and the Fermi energy along the ingot is charac- 344 terized by two principal features. The first feature is the sta- 345 bilization of the free hole concentration and of the 346 galvanomagnetic parameters of the samples from the middle 347 part of ingot due to the pinning of the Fermi level by the res- 348 onant Fe-induced level. This is quite expected and typical 349 for all previously investigated PbTe-based alloys doped with 350 group III (In, Ga), rear earth (Yb), and transition metal (Sc, 351 Ti, V, Cr) impurities. The second feature is the p-n inversion 352 of the conductivity type with a subsequent increase in the 353 concentration of free electrons, i.e., the breakdown of pin- 354 ning of the Fermi level at the end of the ingot. This effect 355 has previously been observed only in heavily doped 356 $Pb_{1-v}V_{v}Te^{23}$ and, possibly, in $Pb_{1-v}Ti_{v}Te$ alloys.³⁴ A com- 357 parison of the kinetics of changes in the concentration of 358 charge carriers in PbTe-based alloys doped with impurities 359 of transition metals, recently made by us in Ref. 19, suggests 360 that this behavior may be universal for all of the abovemen- 361 tioned doped alloys. Thus, to interpret the experimental 362 results obtained in the present work, we use a model for the 363 reconstruction of the electronic structure upon doping that 364 was previously proposed for $Pb_{1-x-y}Sn_xV_yTe$,²³ and in 365 which we shift the deep donor impurity level from the gap 366 (as it is in $Pb_{1-v}V_{v}Te$) to the valence band (as it is in 367 $Pb_{1-y}Fe_{y}Te$) (Fig. 7). 368

According to this model, assuming a monotonous $_{369}$ increase of the impurity content along the ingot, the kinetics $_{370}$ of changes of the free carrier concentration and of the Fermi $_{371}$ energy with doping in Pb_{1-y}Fe_yTe may be interpreted as fol- $_{372}$ lows (see Fig. 7). Doping of PbTe with iron results in two $_{373}$ types of resonant donor states. The concentration of the latter $_{374}$ rises gradually along the ingot. The main impurity-induced $_{376}$ band, while the additional resonant donor level E_i is some- $_{377}$ where in the conduction band, well above its bottom. $_{378}$



FIG. 7. Model for the rearrangement of the electronic structure of $Pb_{1-y}Fe_yTe$ upon doping assuming the appearance of a resonant iron level E_{Fe} under the bottom of the valence band and of an additional donor-type resonant level of intrinsic point defects E_i in the conduction band.

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Initially (see left panel in Fig. 7), an increase in the concen-379 tration of donor resonant states of both types along the ingot 380 induces the filling of the valence band states that lie below 381 the main impurity-induced resonant level $E_{\rm Fe}$, a decrease of 382 383 the free hole concentration, and a shift of the Fermi level upwards until the pinning of the Fermi energy inside the im-384 385 purity band. Then (see central panel in Fig. 7), long sections of stabilization of concentration of free holes and of the 386 Fermi level, associated with the gradual filling of the impu-387 388 rity band with electrons from the donor level E_i , take place. However, filling of the impurity band with electrons leads to 389 390 a breakdown of pinning of the Fermi level and to fast filling of the upper valence band states. Finally (see right panel in 391 392 Fig. 7), subsequent increase in the concentration of resonant donor states in the conduction band induces a p-n-conver-393 sion, an increase in the concentration of free electrons, and a 394 395 shift of the Fermi level upwards into the conduction band due to the flow of electrons from the donor level E_i to the 396 397 conduction band.

Thus the appearance of the main impurity level $E_{\rm Fe}$ 398 399 upon doping provides a possibility of stabilization of the Fermi level in a finite range of impurity concentrations. At 400 the same time, the generation of additional donor levels in 401 the conduction band leads to filling of the impurity band in 402 403 the region of Fermi level stabilization, to a breakdown of 404 pinning of the Fermi level, and to a *p*-*n* inversion of conductivity type in the alloys upon further doping. However, it 405 should be noted that this model implies a monotonous 406 increase in the impurity concentration in the main phase 407 408 along the ingot. At the same time, as we have already noticed in Section III, the iron impurity concentration in the main 409 phase only slightly rises in the whole investigated part of the 410 ingot (samples 20 to 2), most likely due to the fact that the 411 limit of solubility of impurities has already been reached in 412 the middle part of the ingot. On the other hand, the total con-413 centration of iron in the samples continues to change and 414 increases dramatically at the end of the ingot, resulting in the 415 formation of inclusions of second phase, which are similar in 416 417 composition to compounds of impurity atoms with tellurium. In turn, the formation of such inclusions should lead to a vio-418 lation of the stoichiometric composition of the main phase, 419 to a depletion of atoms of tellurium and as a consequence to 420 421 an increase in the concentration of tellurium vacancies and 422 of interstitial atoms of lead in the main phase.

These facts allow us to conjecture that additional donor 423 states in the conduction band are not directly related to the 424 presence of iron in the alloys. Most likely they originate 425 426 from a deviation from the stoichiometric composition in the main phase and represent levels of intrinsic point defects 427 with concentrations gradually changing along the single-428 crystal ingot. Then an increase in the concentrations of tellu-429 rium vacancies and of interstitial lead atoms, that according 430 to the well-known theoretical conceptions^{31,35-40} and experi-431 mental data^{31,41,42} induce donor-type resonant states deep in 432 433 the conduction band (for example, three levels due to a tellurium vacancy split off from the valence p-bands), takes 434 435 place. This leads to a breakdown of pinning of the Fermi level and to a growth of free electron concentration in the 436 437 main phase at the end of ingot. We believe that this J. Appl. Phys. **118**, 000000 (2015)

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explanation is of a general nature and can be used to describe 438 the kinetics of changes in the concentration of charge carriers 439 in all heavily doped PbTe-based semiconductors with transition metal impurities provided that the solubility limit of impurity is reached. 442

VI. CONCLUSIONS

Our x-ray phase and x-ray fluorescence analysis shows 444 that $Pb_{1-y}Fe_yTe$ alloys synthesized by the Bridgman method 445 contain microscopic inclusions enriched with iron as well as 446 regions of a second phase with a chemical composition close 447 to FeTe. In the main phase which has good uniformity, the 448 iron impurity content only slightly rises along the ingot 449 reaching the impurity solubility limit at approximately 450 0.6 mol. % already in the middle of the ingot, whereas integral iron content continues to change, increasing sharply at 452 the end of the ingot. 453

At the same time, galvanomagnetic parameters as well 454 as the concentration of free charge carriers in the samples 455 change by orders of magnitude along the ingot, as if the con- 456 centration of iron impurity monotonically increased along 457 the axis of the ingot. First we observe a decrease in the con- 458 centration of free holes and its saturation at a level of 459 approximately $6 \times 10^{17} \text{ cm}^{-3}$ associated with the pinning of 460 the Fermi level by the iron-induced resonant level $E_{\rm Fe}$, situ- 461 ated under the top of the valence band. In these samples, the 462 temperature dependences of the Hall coefficient are anoma- 463 lous in nature, which also indicates the pinning of the Fermi 464 level by the resonant impurity level. Then, after a long 465 region of stabilization of galvanomagnetic parameters, a 466 breakdown of pinning of the Fermi level, a p-n inversion of 467 the conductivity type, and an increase in concentration of 468 free electrons in the samples take place. 469

Kinetics of changes in the free charge carrier concentra- 470 tion and in the Fermi energy relative to the band edges along 471 the $Pb_{1-v}Fe_vTe$ ingot is calculated and analyzed. By apply- 472 ing the six-band Dimmock dispersion relation for IV-VI 473 semiconductors to galvanomagnetic data, the position of 474 the Fe-induced resonant level measured from the top of the 475 valence band at liquid-helium temperature $(E_v - E_{Fe} \approx 476)$ 16 meV) is determined. We assume that the breakdown of 477 pinning of the Fermi level and the p-n inversion of the con- 478 ductivity type are not directly related to the presence of iron 479 in the alloys. They may be associated with depletion of the 480 main phase of tellurium atoms due to formation of micro- 481 scopic inclusions of a second phase enriched with tellurium 482 and violation of the stoichiometric composition of the main 483 phase. It is quite possible that the formation of inclusions 484 enriched with iron when doping ensures preservation of the 485 high homogeneity of the main phase of $Pb_{1-v}Fe_vTe$ crystals. 486

We explain our experimental results using the model of 487 electronic structure rearrangement upon doping, a model 488 similar to the one suggested earlier for vanadium-doped 489 PbTe-based alloys, replacing the impurity-induced deep 490 level in the gap (as it is in $Pb_{1-y}V_yTe$) with the one in the valence band (as it is in $Pb_{1-y}Fe_yTe$). According to this model, 492 doping of PbTe with iron introduces two different donor-like 493 resonant levels E_{Fe} and E_i lying under the bottom of the 494

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valence band and deep in the conduction band, respectively. 495 The impurity level $E_{\rm Fe}$ provides the filling of the valence 496 497 band with electrons and the pinning of the Fermi level in a wide range of impurity concentrations while the additional 498 level E_i , the nature of which is not yet clear, ensures the 499 breakdown of the Fermi level pinning, the *p*-*n* conversion, 500 and the increase in the concentration of free electrons at the 501 end of the ingot. We conjecture that due to the change in the 502 stoichiometric composition and to the depletion of tellurium 503 504 atoms in the main phase along the ingot, the role of resonant donor levels E_i can be played by the levels of intrinsic point 505 defects (tellurium vacancies and lead interstitials) lying deep 506 in the conduction band and having a donor nature. 507

508 As a final remark, we would like to note that, in our opin-509 ion, the model of electronic structure rearrangement of Pb_{1-v}Fe_vTe with doping is general and can be used for PbTe-510 based alloys doped with other impurities of transition metals. 511

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