KNIGHT SHIFT AND CRITICAL POINTS IN THE BAND SPECTRUM OF PbTe AND SnTe

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We study the Knight shift (ΔH) on nuclei ^{207}Pb in PbTe (of the n- and p-type) and on ^{119}Sn in p-SnTe in a maximally wide region of the concentrations of current carriers. In the samples of p-PbTe in the interval of concentrations $6\times10^{16} \le p < 6.6\times10^{19}$ cm^{-3} ($p = p_{77}$), the shift is diamagnetic. For $p \approx 2\times10^{19}$ cm^{-3}, ΔH attains the maximum value, and, for $p \approx 6.6\times10^{19}$ cm^{-3}, the sign of ΔH is inverted. In n-PbTe, we observe the paramagnetic Knight shift which weakly depends on the concentration of electrons in the interval $6.2\times10^{16} \le n < 2\times10^{19}$ cm^{-3}. For $n \approx 2\times10^{19}$ cm^{-3}, a sharp jump of ΔH by ≈ 60 Gs happens. In SnTe, the shift $\Delta H > 0$ in the interval $p = 0.6\times p_{77} = 3.3\times10^{19} \div 2.24\times10^{21}$ cm^{-3}, and the dependence $\Delta H(p)$ has a nonmonotonous character. In view of the concentration dependences of the Knight shift, we established the existence of critical points in the band spectra of SnTe and PbTe.

1. Introduction

Semiconducting compounds of the A^4B^6 type are successfully used in infrared optoelectronics. The perspectives of their application are significantly extended upon the use of modern nanotechnologies of the formation of quantum dots in multilayer structures.

The energy spectrum of these compounds is well studied in the region of the low concentrations of current carriers. In particular, to explain the concentration and temperature dependences of kinetic coefficients, the two-band model of the valence band of p-PbTe is used (with regard for the L- and Σ-bands) [1]. But already the first studies of the nuclear magnetic resonance (NMR) of lead telluride showed that this model is of little use for the explanation of experimental data, especially in the region of high concentrations [2].

Indeed, it was shown in the theoretical works [1, 3] that the valence band of compounds A^4B^6 in the cubic phase has a complicated structure. In particular, the existence of 5 critical points in the band spectrum of holes was foreseen, and the fundamental possibility to find the singular points of a spectrum by using the concentration and temperature dependences of the magnetic susceptibility $\chi(n,T)$ [3] was established. It turned out that the singular points (and their type), which were observed on the concentration dependences of the density of states and the magnetic susceptibility, coincide.

Upon the passage of the Fermi level through the critical points of the band spectrum, the qualitative reconstruction of the spectrum of current carriers near the Fermi level is realized. A change of the Fermi surface topology causes the corresponding variation of the density of states ν (where ν is a function of the energy) and, as a result, a change of thermodynamic quantities [3]. Hence, upon the filling of the band by carriers up to the critical energies, we will observe the peculiarities related to the passage of the Fermi level through the singular points of the spectrum on the concentration dependences of ν and χ. The experimental confirmation of the theory was presented in [4]. It is established that the concentrations, for which 3 breaks are seen on the dependence χ_{40K}(p), correspond to 3 critical points (from 5 points foreseen by the theory) in the valence band of SnTe.

The Knight shift (an additional magnetic field on a nucleus caused by the electron-nucleus interaction) in degenerate semiconductors is directly connected, like χ, with the density of states on the Fermi level. Therefore, we consider that the changes in the density of states, which are related to a change of the Fermi surface topology, must be also revealed on the concentration dependence of the Knight shift (ΔH).

In the present work, we investigate the concentration dependences of the Knight shift on nuclei ^{207}Pb in PbTe of the n- and p-type and on ^{119}Sn in p-SnTe in a wide interval of the concentrations of free carriers. The critical points in the spectrum of SnTe, which are determined by the dependence $\Delta H(p)$, well agree with those obtained in [4]. This allows us to analyze the features of the band structure in lead tellurides, by using the concentration dependences $\Delta H\ (n,p)$.

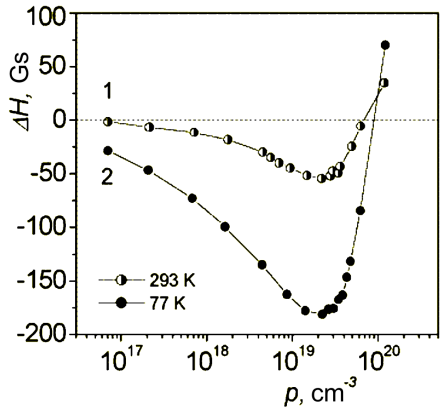

Fig. 1. Dependences of the Knight shift on nuclei ^{207}Pb on the concentration of holes in p-PbTe for two temperatures

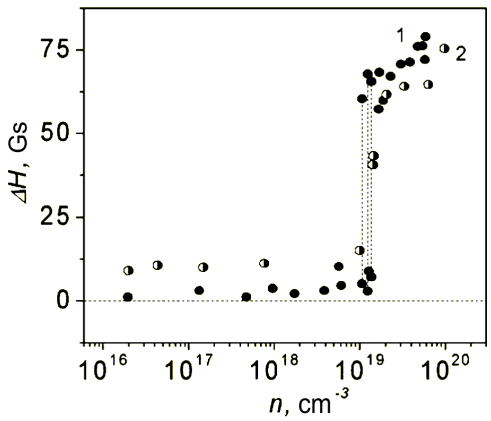

Fig. 2. Dependences of the Knight shift on nuclei ^{207}Pb on the concentration of electrons in n-PbTe (*1*) and in $Pb_{0.94}Ge_{0.06}Te$ (*2*) at $T = 293$ K

2. Experiment

For the recording of NMR signals, we used the procedure proposed in [5]. The particular structure of a gage of the inductive type ensured the long-term stable balance and a high level of the isolation of a transmitter and a receiver (up to 100 dB) for the sufficiently high intensity of a high-frequency field ($H_1 = 0.3$ Gs).

The recording of spectra was carried out at a constant frequency of 13.495 MHz by means of the rapid scanning of the conditions of a resonance with the registration of the absorption line. Upon the observation of wide spectra (>10 Gs), we applied the modulation technique with slow passage and the recording of derivatives of the NMR line. In both cases, we use the digital accumulation of resonance spectra in order to improve the signal/noise ratio. To eliminate the influence of a plastic deformation on the spectra of ^{207}Pb in p-PbTe [6], the study was carried out on monocrystalline plates 100—200 μm in thickness. At the same time, the grinding of a material practically has no effect on the line form and the Knight shifts in n-PbTe and SnTe.

The measurement of the Hall effect was performed by the standard 4-probe method at a constant current and a constant magnetic field [7].

3. Experimental Results

3.1. Knight shift in PbTe of the p- and n-type

The measurements of the Knight shift in p-PbTe were performed at $T = 293$ and 77 K in the interval of the concentrations of holes $p = p_{77} = 6 \times 10^{16} \div 2 \times 10^{20}$ cm^{-3}. The samples with a minimum concentration were obtained by means of the annealing in vapors of a metal or chalcogen, and those with higher concentrations were produced with the help of the doping of PbTe by impurities of Li, Na, and Tl.

In Fig. 1, we give the dependence $\Delta H(p)$ in p-PbTe. The shift was determined as the difference between the total resonance field on a nucleus and the reference magnetic field [$H_{\rm et} = (15135 \pm 2)$ Gs, $T = 293$ K]. The field $H_{\rm et}$ which corresponds to the chemical shift on ^{207}Pb in p-PbTe was determined by means of the extrapolation of the concentration dependence of the resonance field to the minimum values of p.

In the region of concentrations $6{\times}10^{16} \le p < 6.6 \times 10^{19}$ cm^{-3}, the Knight shift is negative, i.e. it is diamagnetic. For $p \approx 2.3 \times 10^{19}$ cm^{-3}, it attains the maximum value, and, for the concentration $p \approx 6.6 \times 10^{19}$ cm^{-3} and at $T = 293$ K, we observe the inversion of the sign of ΔH.

The dependence ΔH (n) on nuclei ^{207}Pb in n-PbTe has a quite different character (Fig. 2). In the region $6{\times}10^{16} \le n < 2 \times 10^{19}$ cm^{-3} (where $n = n_{77}$), ΔH depends weakly on the concentration of electrons. However, near $n_{\rm cr} \approx 2 \times 10^{19}$ cm^{-3}, we see first a sharp jump of the Knight shift (approximately by 60 Gs) which is accompanied by the broadening of resonance lines (>10 Gs) and by a significant reduction of the duration of the spin-lattice relaxation (T_1).

The transient region is characterized by the presence of complicated spectra which are mostly composed from two lines, the distance between which being equal to a value of the jump. In addition, in the region of low concentrations n, the saturation of NMR occurs already

at the value of the radio-frequency field $H_1 \approx 10$ mGs, whereas it is absent for $n > n_{cr}$ even for $H_1 > 100$ mGs. As distinct from p-PbTe, the Knight shift in n-PbTe is paramagnetic in the entire region of concentrations (Fig. 2, curve *1*). An analogous dependence ΔH (n) is established also in n-$Pb_{0.94}Ge_{0.06}Te$ (curve *2*).

3.2. Knight Shift in SnTe

For the first time, the study of the NMR spectra on nuclei ^{119}Sn and ^{125}Te in SnTe was performed in [8]. The reference field on nuclei ^{119}Sn is $H_{et} = 8514$ Gs. In the present work, we investigated comprehensively the dependence ΔH (p) on ^{119}Sn in the interval $p = 3.3 \times 10^{19} \div 2.24 \times 10^{21}$ cm^{-3} $(p = 0.6 \times p_{77}$ [4]). Since the ferroelectric phase transition occurs in SnTe for $p < 8 \times 10^{20}$ cm^{-3} at $T < 150$ K and the rhombohedral phase is formed [1], the resonance fields were measured at $T = 293$ K.

As seen from Fig. 3, the shifts increase nonmonotonously with the concentration of holes. The well-pronounced breaks are observed for $p_1 = 1.05 \times 10^{20}$ cm^{-3}, $p_2 = 2.28 \times 10^{20}$ cm^{-3}, and $p_3 = 6.0 \times 10^{20}$ cm^{-3}. For $p > 6.0 \times 10^{20}$ cm^{-3}, the Knight shift on ^{119}Sn exceeds its value in metallic tin.

Arrows *1,2*, and *3* correspond to the concentrations $p_1 = 1.05 \times 10^{20}$, $p_2 = 2.28 \times 10^{20}$, and $p_3 = 6.0 \times 10^{20}$ cm^{-3}. The arrow $Sn(m)$ indicates the Knight shift in metallic tin.

4. Discussion of Results

At present, there is no theory which would clarify the concentration dependences of the Knight shift in a wide interval of the concentrations of carriers, including high concentrations (10^{20}—10^{21} cm^{-3}). First of all, this is related to the absence of a sufficient volume of experimental studies. For example, in works [9, 10], the dependences ΔH (n, p) on nuclei ^{207}Pb in PbTe were investigated only for the concentrations of carriers $p \leq 2 \times 10^{19}$ cm^{-3}. It is worth to note that we have first studied the Knight shift on ^{207}Pb and ^{119}Sn in PbTe and SnTe up to the maximum concentration of carriers for these compounds.

The results obtained by us in the region of low concentrations $p \leq 2 \times 10^{18}$ cm^{-3}(Fig. 1) can be explained on the basis of the simple band моделі [9, 10]. It is known that the wave functions L_6^+ describing the top of the valence band have the significant s-component at sites ^{207}Pb. Therefore, the additional magnetic field (ΔH) created by free carriers on ^{207}Pb

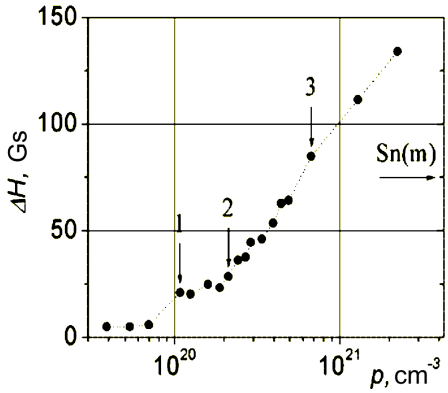

Fig. 3. Concentration dependence of the Knight shift on nuclei ^{119}Sn in SnTe at $T = 293$ K

is caused by the contact hyperfine Fermi interaction. In this case, the formula for the Knight shift looks as [10]

$$\Delta H_{cont} = \frac{4}{3} g_s g_v \mu_B^2 \rho_v(E_f)(\cos^2\theta^+)\langle R|\Delta r|R\rangle, \qquad (1)$$

where g_s is the g-factor of a free electron, g_v is the effective g-factor of carriers of the valence band, $\rho_v(E_f)$ is the density of states on the Fermi level, μ_B is the Bohr magneton, and the factor $(\cos^2\theta^+)\langle R|\Delta r|R\rangle$ is the relativistic equivalent of $|\psi(0)|^2$ which defines the probability of the presence of carriers at nuclear sites. In this case, the diamagnetic character of the Knight shift on ^{207}Pb in p-PbTe (Fig. 1) is conditioned by the negative sign of components of the effective g-factor of holes ($g_{\|}^v = -48 \pm 5$ and $g_{\perp}^v = -19.6$) [10].

In the region of higher concentrations, $3 \times 10^{18} \leq p < 2 \times 10^{19}$ cm^{-3}, it was proposed in [9, 10] to consider the influence of the nearest bands on the formation of the hyperfine field on ^{207}Pb, without taking the Σ-band into account. Such an influence is manifested in the mixing of states of the valence band and the nearest conduction band, whose electrons are mainly in p-states. Due to relativistic effects, the hyperfine fields on ^{207}Pb induced by the spin-orbit (ΔH_{orb}) and dipole-dipole (ΔH_{dip}) interactions can exceed the contact field ΔH_{cont} which appears for low values of p.

But, even in the framework of the two-band model [11], it is impossible to explain the sign inversion of ΔH in p-PbTe (Fig. 1). In the other case, it is necessary to assume that the hyperfine fields which are created by holes of the L- and Σ-bands on ^{207}Pb have opposite signs. With increase of the concentration p, the shift ΔH will be defined mainly by the parameters of the spectrum of holes of the Σ-band. But the large shifts

ΔH in this case mean the presence of carriers in the Σ-band with large effective g-factors and thus with small effective masses, which does not agree with the known data ([1], see references [5—8]).

Like in the case of p-PbTe, the behavior of the dependence ΔH (n) in n-PbTe in the interval $6{\times}10^{16} \leq n{<}2{\times}10^{19}\mathrm{cm}^{-3}$ (Fig. 2) can be described by the simple band model [9]. But the sharp jump on the dependence ΔH (n) near $n \approx 2 \times 10^{19}$ cm^{-3} requires new ideas of the structure of the conduction band in n-PbTe. Such a jump of ΔH, which is accompanied by the broadening of NMR lines and by a significant reduction of the duration of the spin-lattice relaxation T_1, can be related to the critical change of parameters of the energy spectrum in the conduction band. In this case, we observed no peculiarities in the kinetic parameters of specimens, and the X-ray diffraction analysis showed the invariability of the crystal lattice constant (prior to and after the jump) in the limits of errors $\delta = \pm 0.0005$ Å.

In view of the above-written, of special interest (as for the comprehension of the features of the band structure of PbTe) is the analysis of the concentration dependence of ΔH on nuclei ^{119}Sn in SnTe. This is explained by the fact that a model of the complicated structure of the valence band which was proposed for compounds A^4B^6 in [1,3] was experimentally confirmed [4] namely on SnTe. The discovered peculiarities in the form of breaks on the concentration dependence of the magnetic susceptibility $\chi(p)$ for $p_{c1} = 1.1 \times 10^{20}$ cm^{-3}; $p_{c2} = 2.3 \times 10^{20}$ cm^{-3}, and $p_{c3} = 4.9 \times 10^{20}$ cm^{-3} [4] are identified as the van Hove peculiarities which correspond to the Σ-extremum, the saddle point firstly observed in the ΣL direction, and the Δ-extremum of the valence band.

As seen from Fig. 3, the dependence $\Delta H(p)$ in SnTe possesses also 3 breaks for the concentrations $p_1 = 1.05 \times 10^{20}$ cm^{-3}, $p_2 = 2.28 \times 10^{20}$ cm^{-3}, and $p_3 = 6 \times 10^{20}$ cm^{-3} which correspond to the critical points of the spectrum established in [4]. In addition, there exists the correlation between the dependences $\Delta H(p)$ and $g(p)$ (the density of states calculated in [4]). Thus, two independent methods (χ and NMR) confirmed the existence of 3 singular points in the valence band of SnTe. The changes in the density of states related to a variation of the Fermi surface topology are manifested on both the concentration dependences $\chi(p)$ and $\Delta H(p)$.

We can now carried out the analysis of each of the linear sections of the curve $\Delta H(p)$ with regard for the character of the dependence $\chi(p)$ in various concentration intervals [4].

According to the inversion model, the symmetry of bands in SnTe is inverted relative to that in PbTe [11]. The wave functions which describe the top of the valence band in SnTe have the p-component at sites ^{119}Sn. Just this fact explains the small Knight shifts (∼2.5 Gs) on the first linear section $3.3{\times}10^{19} < p \leq 8.4 \times 10^{19}$ cm^{-3} which corresponds to the L-band.

On the second section $1.05{\times}10^{20} < p < 2.28 \times 10^{20}$ cm^{-3} ($p_1 < p < p_2$), the shifts are mainly due to the hyperfine interaction of nuclei with holes of the Σ-band. In view of the great diamagnetism of holes in the Σ-band [4], we can conclude that a source of the Knight shifts on ^{119}Sn in the Σ-band is the orbital hyperfine interaction.

The significant concentration dependence of shifts (and of the width of the lines, whose form deviates from the Gauss one [8]) is observed on the third section $2.28{\times}10^{20} < p < 6.0 \times 10^{20}$ cm^{-3} ($p_2{<}p{<}p_3$). We see the sharp reduction of the diamagnetic component of χ [4], which is equivalent to the increase in the Pauli paramagnetism. By the data in [4], the Fermi surface in SnTe becomes open, like in metals, for the concentration $p = p_{c2} = 2.3 \times 10^{20}$ cm^{-3} which corresponds to the saddle point in the spectrum of holes. The field shift on ^{119}Sn not only attains the value characteristic of metallic tin, but exceeds it. The last fact testifies to a significantly greater density of wave functions of the s-type on nuclei ^{119}Sn in SnTe as compared with the atomic value.

The fourth concentration interval $6.0{\times}10^{20} < p < 2.24 \times 10^{21}$ cm^{-3} ($p > p_3$) corresponds to the Δ-band, whose holes are paramagnetic [4]. Here, we observe a great growth of ΔH on ^{119}Sn (from 82 to 140 Gs), which confirms the conclusion that the Fermi surface in SnTe is open for $p \geq 2.3{\times}10^{20}\mathrm{cm}^{-3}$.

Thus, the correlation established between the dependences $\chi(p)$ and $\Delta H(p)$ in SnTe testifies to a possibility to find the critical points of the spectrum in compounds A^4B^6 by using the concentration dependences of the Knight shift. The absence of theoretical and experimental studies of the band structure of PbTe in the region of high concentrations (n, $p > 2 \times 10^{19}$ cm^{-3}) does not allow us to perform the detailed analysis of the dependence $\Delta H(n,p)$ which would be analogous to that executed for SnTe. But the obtained results testify unambiguously to the complicated structure of not only the valence band in PbTe, but the conduction band as well.

For example, the peculiarities which are revealed on the dependence ΔH (p) in p-PbTe (the extremum for $p \approx 2.3 \times 10^{19}$ cm^{-3} and the shift sign inversion at $T = 293$ and 77 K in Fig. 1) can be related only to a change of the density of states upon the passage of the

Fermi level through the critical points of the spectrum of holes in p-PbTe. It is quite probable that the Fermi surface becomes open for $p > 6.6 \times 10^{19}$ cm^{-3} ($T = 293$ K), because we observe a further increase of ΔH with p. The formation of the open Fermi surface for $n > 2 \times 10^{19}$ cm^{-3} can also explain the jump of ΔH in n-PbTe and in the solid solution n-$Pb_{0.94}Ge_{0.06}Te$ (Fig. 2).

5. Conclusions

1. By the example of SnTe, we have shown the possibility to determine the critical points of the band spectrum by using the concentration dependence of the Knight shift. We have established the existence of 3 critical points in the spectrum of holes in SnTe for $p_1 = 1.05 \times 10^{20}$ cm^{-3}, $p_2 = 2.28 \times 10^{20}$ cm^{-3}, and $p_3 = 6.0 \times 10^{20}$ cm^{-3} which well agree with those discovered in [4] for the concentration dependence of the magnetic susceptibility χ(p).

2. The peculiarities which were first observed on the curves ΔH(p) in p-PbTe (in the form of an extremum and the sign inversion of ΔH) correspond to the critical points of the the valence band for $p_1 \approx 2 \times 10^{19}$ cm^{-3} and $p_2 \approx 6.5 \times 10^{19}$ cm^{-3}. In this case, we assume that the Fermi surface in p-PbTe becomes open for $p_{77} > 6.6 \times 10^{19}$ cm^{-3} ($T = 293$ K).

3. The sharp jump of ΔH observed for the first time in n-PbTe near $n_{\rm cr} \approx 2 \times 10^{19}$ cm^{-3} testifies to a critical change of parameters of the energy spectrum in the conduction band, which leads to the appearance of the open Fermi surface for $n > 2 \times 10^{19}$ cm^{-3}.

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ЗСУВ НАЙТА І КРИТИЧНІ ТОЧКИ В ЗОННОМУ СПЕКТРІ PbTe ТА SnTe

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Р е з ю м е

Проведено дослідження зсуву Найта ΔH на ядрах ^{207}Pb в PbTe (n- і p-типу) і ^{119}Sn в p-SnTe в максимально широкій області концентрацій носіїв струму. Виявлено, що в зразках p-PbTe в інтервалі концентрацій $6{\cdot}10^{16} \le p < 6,6 \cdot 10^{19}$ см$^{-3}$ ($p = p_{77}$) зсув є діамагнітним. При $p \approx 2 \cdot 10^{19}$ см$^{-3}$ ΔH досягає максимального значення, а при $p \approx 6,6 \cdot 10^{19}$ см$^{-3}$ спостерігається інверсія знака ΔH. В n-PbTe спостерігається парамагнітний зсув Найта, який слабо залежить від концентрації електронів в інтервалі $6,2 \cdot 10^{16} \le n < 2 \cdot 10^{19}$ см$^{-3}$, а при $n \approx 2 \cdot 10^{19}$ см$^{-3}$ відбувається різкий стрибок ΔH приблизно на 60 Гс. В SnTe зсув $\Delta H > 0$ в інтервалі $p = 0,6p_{77} = 3,3{\cdot}10^{19} \div 2,24{\cdot}10^{21}$ см$^{-3}$ і залежність $\Delta H(p)$ має немонотонний характер. Виходячи із концентраційних залежностей зсуву Найта, встановлено існування критичних точок у зонних спектрах SnTe та PbTe.