STUDY OF DEFECTS IN GeTe
AND (GeTe)$_{1-x}$(AgBiTe$_2$)$_x$ SOLID SOLUTIONS
BY POSITRONS

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Positron lifetimes and Doppler broadening of the annihilation line measurements were performed to study the vacancy type defects in polycrystalline GeTe and (GeTe)$_{1-x}$(AgBiTe$_2$)$_x$ ($x = 0, 0.03, 0.05, 0.1, 0.15, 0.2$, and 1) solid solutions. The values of lifetimes obtained are explained as due to positron and positronium saturated trapping at vacancies and vacancy clusters. The interdependence between mean positron lifetime and hole concentration is discussed.

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1. Introduction

Positron annihilation spectroscopy (PAS) has often been used to study the defect structure of Ge, Si, III–V, and II–VI compound semiconductors [1–5]. No systematic PA studies have been performed for studying the defects in IV–VI compounds. Only PbTe [6], PbSe, and Pb$_{1-x}$Sn$_x$Te are studied by positrons [7].

GeTe is a narrow band gap semiconductor of $p$-type. According to [8] the acceptors are doubly ionized cation vacancies. Therefore, PAS can be used to study the defect structure of GeTe.

In this paper we report the results of measurements of positron annihilation lifetimes (PAL) and Doppler broadening of annihilation line (DBAL) in GeTe. To our knowledge this is the first application of PAS to study the defect structure of this compound semiconductor. The (GeTe)$_{1-x}$(AgBiTe$_2$)$_x$ solid solutions (SSs) ($x = 0.03, 0.05, 0.1, 0.15, 0.20$, and 1) have also been studied.

2. Experimental

The details of materials synthesis used are given elsewhere [9]. The samples were cut from the respective ingots and were 1.5–2 mm thick. The surfaces facing
the positron source were carefully processed in order to minimize the thickness of
the damaged surface layer.

The lifetime spectrometer was a standard fast-fast coincidence apparatus
with time resolution of \( \approx 260 \, \text{ps FWHM} \). The experimental spectra were fitted
with the program POSITRONFIT-EXTENDED [10].

The Doppler broadening of the 511 keV annihilation \( \gamma \)-line was measured
using a high purity germanium detector of energy resolution 1.17 keV at 514 keV
\( \gamma \)-line of \( ^{85}\text{Sr} \). The annihilation \( \gamma \)-line was characterized with usual shape \( S \) and
\( W \)-parameters. All measurements were made at room temperature.

### 3. Results and discussion

Positron spectra were decomposed into two and three terms. The mean
positron lifetimes \( \tau_m \) \( (\tau_m = \sum_{i=1}^{3} I_i \tau_i) \) coincide in the error limits (Table). They
increase with the increase in the \( \text{AgBiTe}_2 \) content denoted \( x \). As the three-component
fit resulted into \( \chi^2 \) values of the order of \( 1 \), or less than \( 1 \), the interpretation
of positron states is based on this fit. The obtained lifetimes \( \tau_i \) and their relative
intensities \( I_i \) are shown in Table.

<table>
<thead>
<tr>
<th>No.</th>
<th>( x )</th>
<th>( \tau_1 ) [ps]</th>
<th>( I_1 ) [%]</th>
<th>( \tau_2 ) [ps]</th>
<th>( I_2 ) [%]</th>
<th>( \tau_3 ) [ps]</th>
<th>( I_3 ) [%]</th>
<th>( \tau_m ) [ps]</th>
<th>( \tau_m ) [ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>244.8(4)</td>
<td>77.8(3)</td>
<td>446(4)</td>
<td>17.2(3)</td>
<td>2180(3)</td>
<td>5.0(1)</td>
<td>376.6(5)</td>
<td>375.2(2)</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>261(3)</td>
<td>79(2)</td>
<td>433(16)</td>
<td>15(2)</td>
<td>2152(14)</td>
<td>5.0(3)</td>
<td>382(12)</td>
<td>383(1)</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>260(1)</td>
<td>84.6(8)</td>
<td>547(23)</td>
<td>8.9(7)</td>
<td>2227(24)</td>
<td>6.6(1)</td>
<td>420(4)</td>
<td>418(1)</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>264(2)</td>
<td>81(2)</td>
<td>484(23)</td>
<td>11(1)</td>
<td>2177(12)</td>
<td>7.2(8)</td>
<td>427(9)</td>
<td>427(1)</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>261(1)</td>
<td>81(1)</td>
<td>500(16)</td>
<td>12(1)</td>
<td>2181(16)</td>
<td>7.5(1)</td>
<td>432(7)</td>
<td>431(1)</td>
</tr>
<tr>
<td>6</td>
<td>0.20</td>
<td>263(1)</td>
<td>80.3(5)</td>
<td>535(12)</td>
<td>11.7(5)</td>
<td>2219(16)</td>
<td>7.9(5)</td>
<td>451(4)</td>
<td>447(1)</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>214(1)</td>
<td>81.4(3)</td>
<td>497(5)</td>
<td>11.4(3)</td>
<td>2216(13)</td>
<td>7.1(6)</td>
<td>390(2)</td>
<td>385(1)</td>
</tr>
</tbody>
</table>

As can be seen, the lifetimes cannot be considered as weighted-mean values,
obtained from pure \( \text{GeTe} \) and \( \text{AgBiTe}_2 \). This is not unexpected as the studied
materials are solid solutions of their constituents.
The bulk positron lifetimes $\tau_B$ in GeTe or GeTe-SSs have never been measured or theoretically estimated. The only theoretical estimation, to our knowledge, of the bulk lifetimes in IV–VI compounds semiconductors is given in [7] for PbS, PbSe, and PbTe. If a linear dependence between the bulk lifetimes and the volume per atom, $\Omega$, is considered in the lattice [4, 11], the estimated value of $\tau_B$ for GeTe is $\approx 190$ ps. The values of $\Omega$ were calculated from the data in Ref. [8]. The estimated lifetimes of positrons, trapped at cation and anion vacancies, are $\approx 290$ ps and $\approx 230$ ps, respectively. The values of $\tau_1$(GeTe) = 244.8 ps and $\tau_1$(SSs) $\approx 261$–$266$ ps are much higher than $190$ ps. They could be connected with negatively charged monovacancies in the Ge sublattice. The second lifetime $\tau_2$ $\approx 450$–$550$ ps, most probably, is due to annihilation of positrons, trapped at large vacancy clusters or at surfaces of internal voids (see below).

One of the interesting results from the present measurements is the existence of a long-lived component of the order of $\approx 2.2$ ns with an intensity in the range 5–8%. This implies that Ps atoms are formed in the studied samples. According to [12], positronium formation is impossible in the bulk of semiconductors, but it may occur on the surfaces, including internal ones. Therefore, one could suppose that the studied samples contain free-volume holes (pores). Because of the comparatively high values of mean energy of positrons, emitted from $^{22}$Na ($\approx 0.2$ MeV), and of the intensity $!_3$, $\tau_3$ is unlikely to be connected with the external surface of the chemically etched samples. The intensity of the $\alpha$-Ps component increases versus the increase in AgBiTe$_2$ content, showing that pores are partially connected with the alloying of GeTe. The variations of the two longer lifetimes $\tau_2$ and $\tau_3$ with $x$ are very similar (Table). This could mean that positrons trapped at the surfaces of the pores can annihilate as trapped particles or can form positronium. Therefore, both $\tau_2$ and $\tau_3$ reflect the size of the same pores.

The real composition of GeTe and (GeTe)$_{1-x}$(AgBiTe$_2$)$_x$ solid solutions (GeTe-SSs) can be written as

$$(\text{Ge}_{1-\delta}V^c)V^c \text{Te} \quad \{[(\text{Ge}_{(1-\delta)(1+x)}\text{Ag}_{x/(1+x)}\text{Bi}_{x/(1+x)}]_{1-\delta}V^c\} \text{Te},$$

where $\delta$ is the number of cation vacancies $V^c$. The latter ones are the most probably doubly ionized [8], i.e. they are negatively charged. The respective acceptor levels are located in the valence band. The mechanism of "self-alloying" is the reason for the $p$-type conductivity of the GeTe and the corresponding Ge-rich SSs. The $\delta$-values were estimated by comparison of the densities calculated on the basis of X-ray diffraction results and measured pycnometric ones [13]. For GeTe $\delta = 0.029$. At concentrations of AgBiTe$_2$ below that of vacancy concentration in GeTe, the impurity atoms fill the vacancies and the lattice perfection is improved. At higher AgBiTe$_2$ concentration, the number of the vacancies in GeTe-SSs increases with $x$ from 0.033 to 0.042. Due to this very high concentration of vacancies in the studied materials, one may consider that the trapping of positrons and positronium is saturated, i.e. all of them are trapped before annihilation. This made impossible the use of the trapping model to calculate the rate of the positron trapping at defects.

The hole concentration, $p$, was measured by the Hall-effect experiments at room temperature before positron annihilation measurements. In Fig. 1, the mean
The measured number of carriers is a sum effect of all electrically active centers, present in a sample. In the cited papers, the corresponding carrier concentrations are equal, or directly proportional, to the number of negatively charged vacancies to which positrons are only sensitive. In the present case, the hole concentration decreases...
when the number of the cation vacancies, $\delta$, increases with $x$. In our opinion this is due to creation of donor-type levels, following AgBiTe$_2$ addition. This is consistent with the experimentally observed change of the conductivity from $p$-to $n$-type at $x > 0.1$ [14]. Perhaps, the unusual $\tau_m-p$ dependence is partially explained by decreasing screening length of the $V_{\text{Ge}}$ charge due to extremely high carrier concentration (energy band gap of GeTe $E_g = 0.1$ eV).

Moreover, because of the pores presented in the studied samples, the values of $\tau_m$ strongly depend on the concentration of the pores, as can be seen in Fig. 2, where the interdependence between $\tau_m$ and $I_3$ is presented.

The ranges of variation of $S$ and $W$-parameters are relatively smaller than that observed for other semiconductor compounds. Perhaps, this is due to the fact that the addition of AgBiTe$_2$ does not change the anion sublattice of the GeTe-SSs. Therefore, the nearest surrounding of a cation vacancy $V_{\text{Ge}}$ does not change.

![Graph](image.png)

**Fig. 3.** $W$-parameter as a function of AgBiTe$_2$ content $x$.

The core $W$-parameter as a function of AgBiTe$_2$ amount, $x$, is presented in Fig. 3. The experimental points, except pure GeTe and $x = 0.2$, lie on the same straight line. In our opinion, this is due to the replacing of Ge ions in the cation sublattice with Ag and Bi. In the latter case one can expect more positron annihilations with core electrons.

**4. Conclusions**

Positron lifetimes and DBAL in small band gap semiconductor GeTe and (GeTe)$_{1-x}$(AgBiTe$_2$)$_x$ solid solutions were measured for the first time. It was established that positronium formation occurs in polycrystalline materials studied, and its yield is small ($\approx 5-8\%$) but essential. The shortest lifetime is interpreted as due to positron trapping in negatively charged monovacancies in Ge sublattice. The mean positron lifetime decreases when the hole concentration increases.
References