

# Magnetic properties of $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$ alloys

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**Abstract.** We study the field and temperature dependences of the magnetization ( $B \leq 7.5$  T,  $T = 2.0$ –75 K) of samples from a single crystal  $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$  ( $x=0.08$ ,  $y=0.01$ ) ingot synthesized by the Bridgman method. It is established that the magnetization of the samples contains two main contributions: the Brillouin-type paramagnetism of vanadium ions and the diamagnetism of the crystal lattice. Experimental field and temperature dependences of the magnetization are discussed in the framework of a theoretical model of electronic structure rearrangement in  $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$  with doping and approximated as the sums of two terms based on the modified Brillouin functions for vanadium ions in the  $\text{V}^{3+}$  and  $\text{V}^{2+}$  states. The concentrations of magnetically active vanadium ions in two different charge states with increasing impurity concentration along the ingot are determined.

## 1 Introduction

It is well known that doping of PbTe with vanadium leads to appearance of a deep impurity level  $E_V$  under the bottom of the conduction band ( $E_V \approx E_c - 20$  meV) [1, 2]. When the concentration of tin in  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys rises, the vanadium level slowly moves away from the bottom of the conduction band, remaining inside the forbidden gap for  $x < 0.20$  [3, 4].

As substituting ions in the metal sublattice, vanadium ions initially must be in the electrically neutral  $\text{V}^{2+}$  states. However, since undoped  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys are usually  $p$ -type crystals, the Fermi level is located much lower than the impurity level of vanadium. Therefore, when the concentration of the impurity increases, the self-ionization of the impurity ions takes place ( $\text{V}^{2+} \rightarrow \text{V}^{3+} + e_{\text{band}}$ ) due to the flow of electrons from the impurity level to the valence band [5]. Then, after filling the valence band with electrons, the Fermi level stabilizes inside the impurity band of vanadium, and the concentrations of filled and empty states in this band should become equal to the concentrations of the impurity ions in two different charge and magnetic states:  $\text{V}^{2+}(3d^3)$  and  $\text{V}^{3+}(3d^2)$ , respectively. Thus, the magnetic properties of diluted magnetic semiconductors  $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$  should be determined not only by the impurity concentration, but also by the ratio of the concentrations of vanadium ions in two different magnetic states.

Only the magnetic properties of lead telluride doped with vanadium were investigated previously [6–8]. It was shown that at low temperatures, the field dependences of the magnetization are linear at  $B < 0.5$  T and that the temperature dependences of the magnetic susceptibility follows the Curie–Weiss law. The effective magnetic

moment per vanadium atom does not correspond to any of the possible charge states of vanadium ions and decreases with the increase of vanadium content.

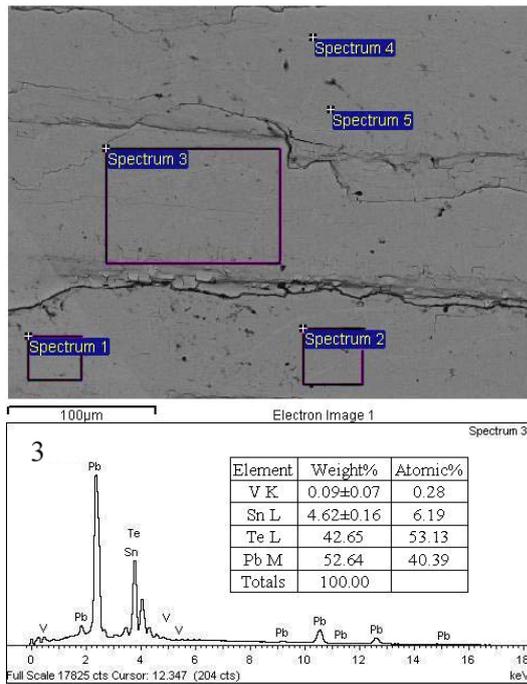
In the present work, we investigate the field and temperature dependences of the magnetization ( $B \leq 7.5$  T,  $2.0 \leq T \leq 75$  K) of samples from a  $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$  ( $x=0.08$ ,  $y=0.01$ ) single-crystal ingot with the variation of the concentrations of tin and vanadium along the ingot. Our main goals are to determine the kinetics of changes in concentration of magnetic ions in two different magnetic states along the ingot and to establish a correlation between the magnetic and galvanomagnetic properties of alloys in the framework of the model of rearrangement of the electronic structure of  $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$  upon doping.

## 2 Experimental details

A single-crystal  $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$  ingot with a nominal tin and vanadium concentrations  $x=0.08$ ,  $y=0.01$  was grown by the vertical Bridgman method [3]. The resulting ingot with its axis roughly corresponding to the  $\langle 111 \rangle$  crystallographic axis, was sliced using a wire saw into 26 wafers approximately 1.5 mm thick (wafer serial numbers are referred below as sample numbers). To determine the composition and to study the magnetic properties of alloys, samples weighing 40 to 80 mg were cleaved from the wafers at the liquid nitrogen temperature.

The phase and elemental composition of the samples were determined using a LEO SUPRA 50VP (Zeiss, Germany) scanning electron microscope equipped with an INCA Energy+ (Oxford Instruments, England) X-ray fluorescence microanalysis system. Figure 1 shows a

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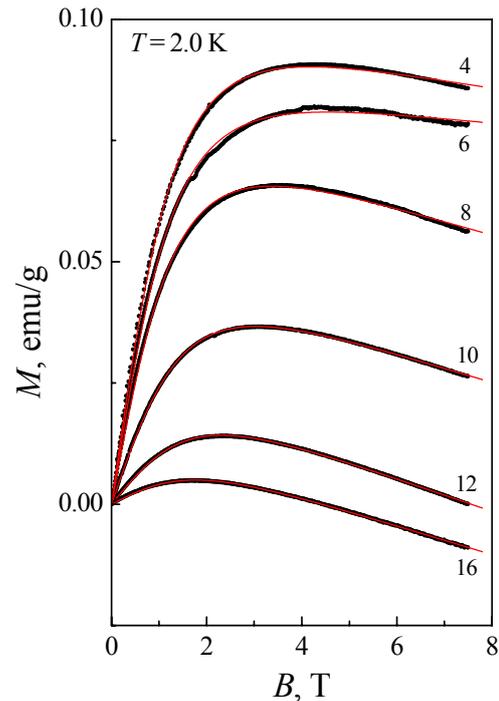
**Fig. 1.** Upper panel: a photograph of the cleavage surface of the sample 3. Lower panel: X-ray emission spectrum for one of the highlighted areas and the elemental composition of the sample.

microphotograph of the cleavage surface and the X-ray emission spectrum for the sample 3, which has Sn content close to the maximum value. We found that all the wafers are rather homogeneous and contain no microscopic inclusions of second phases. The tin concentration increases along the ingot (from sample 26 to sample 2), covering a wide range of  $x$  from 0.05 to 0.18 [3]. The concentration of the vanadium impurity also increases along the ingot but no more than twice, reaching approximately 1.5 mol. %. However, the error in determining the concentration of vanadium is quite large and in the majority of samples comparable with the concentration of vanadium [3].

The magnetization of the samples was studied using a PPMS-9 (Quantum Design, USA) vibrating sample magnetometer. The field dependences of magnetization were measured at several temperatures from 2.0 K to 70 K in fields up to 7.5 T, while the temperature dependences of magnetization – in a constant magnetic field of 1 T and temperatures from 2.0 K to 75 K.

### 3 Results and discussion

The field dependences of the magnetization  $M(B)$  for a series of investigated samples at  $T=2.0$  K are shown in Fig. 2. The analysis of these dependences allow us to conclude that, in contrast to the previously investigated alloys  $Pb_{1-y}Fe_yTe$  [9], in which the impurity level lies in the valence band, the magnetization of  $Pb_{1-x-y}Sn_xV_yTe$  alloys contains only two main contributions. The initial linear increase of the magnetization and its subsequent non-linearity in the region of low temperatures are clearly associated with a Brillouin-type paramagnetic contribution of magnetic  $V^{2+}$  and  $V^{3+}$  ions. At the same



**Fig. 2.** Field dependences of the magnetization for series of investigated  $Pb_{1-x-y}Sn_xV_yTe$  samples at  $T=2.0$  K. Solid lines are theoretical curves calculated according to (2)-(4).

time, the linear decrease of the magnetization at low temperatures and fields  $B>5$  T can be associated with the diamagnetic contribution of the host crystal lattice under conditions of saturation of the paramagnetic contribution of vanadium ions. An increase of vanadium content along the ingot (from sample 16 to sample 4) leads to a significant increase of the paramagnetic contribution, while the diamagnetic contribution of the host lattice remains almost unchanged (see Fig. 2). An increase in temperature leads to a shift of the maximum in the dependence  $M(B)$  towards higher fields and to a linearization of the field dependence of the magnetization typical for the Brillouin-type paramagnetism.

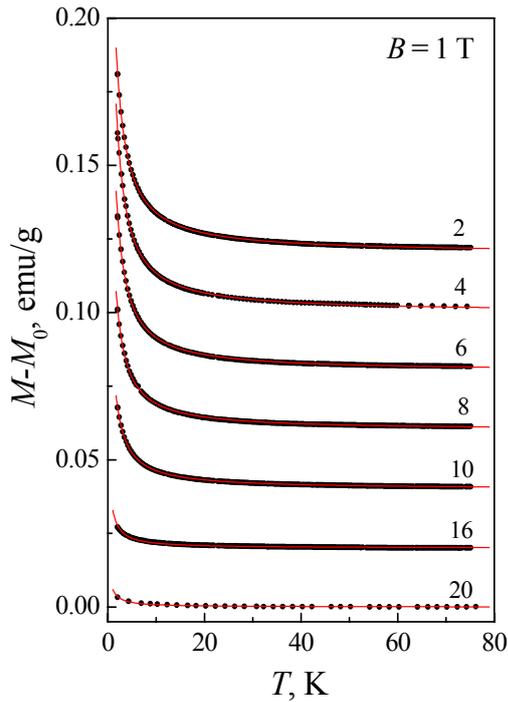
The temperature dependences of the magnetization for series of investigated  $Pb_{1-x-y}Sn_xV_yTe$  samples at  $B=1$  T are presented in Fig. 3. In general, they are of a standard Curie-Weiss type:

$$M(T) = M_0 + \frac{C}{T - \theta} \quad (1)$$

where  $M_0$  is mainly the temperature-independent diamagnetic contribution of the crystal lattice,  $C$  is the Curie constant and  $\theta$  is the Curie temperature.

It is clearly seen that the magnetization at  $T=2.0$  K monotonically increases by more than an order of magnitude with increase of vanadium concentration along the ingot (from sample 20 to sample 2).

Experimental field and temperature dependences of the magnetization are discussed in the framework of the model of the electronic structure rearrangement with doping proposed for  $Pb_{1-x-y}Sn_xV_yTe$  alloys earlier [2, 10]. According to this model, doping leads to the appearance of vanadium ions only in the  $V^{3+}(3d^2)$  state until the



**Fig. 3.** Temperature dependences of the magnetization for series of investigated  $\text{Pb}_{1-x}\text{Sn}_x\text{V}_y\text{Te}$  samples after subtraction of the temperature-independent contribution  $M_0$ . For clarity of presentation, curves 16-2 were consistently shifted upwards with respect to the curve for the sample 20.

pinning of the Fermi level by the vanadium deep level situated under the bottom of conduction band. Only when the Fermi level reaches the impurity level, the self-ionization of  $\text{V}^{2+}$  ions stops and the concentration of vanadium ions in the  $\text{V}^{3+}$  state saturates. Further doping should lead only to the appearance of vanadium ions in the  $\text{V}^{2+}(3d^3)$  state and to a monotonous growth of their concentration.

Our previous results of a galvanomagnetic study of samples from the same  $\text{Pb}_{1-x}\text{Sn}_x\text{V}_y\text{Te}$  ingot [3] indicate that the  $p$ - $n$ -inversion of the conductivity type and pinning of the Fermi level by the vanadium level upon doping occur in the sample 10. So, when constructing the theoretical field dependences of the magnetization in the samples from 20 to 12, we consider the existence of vanadium ions only in the  $\text{V}^{3+}$  state, while in the samples from 10 to 2 – the existence of vanadium ions in two different charge and magnetic states ( $\text{V}^{3+}$  and  $\text{V}^{2+}$ ).

To determine the parameters of  $\text{V}^{2+}$  and  $\text{V}^{3+}$  ions we approximate the  $M(B)$  and  $M(T)$  dependences as sums of two terms based on the modified Brillouin functions [11-13] for two types of impurity ions and temperature-independent contributions linear in magnetic field:

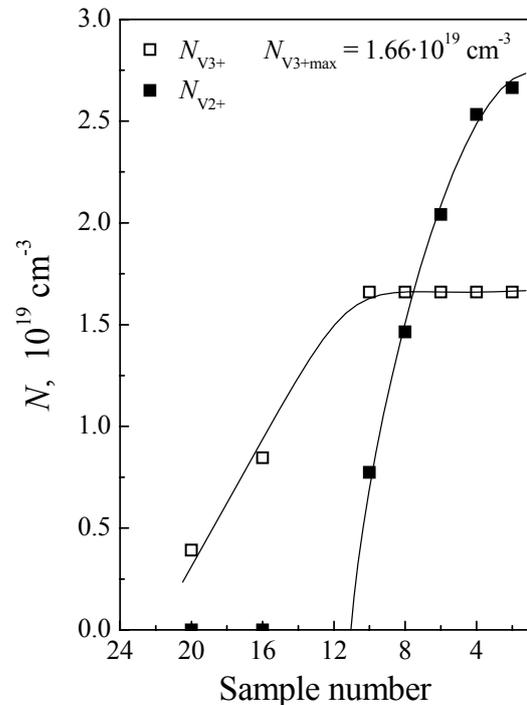
$$M(B, T) = \frac{1}{\rho} \sum_{i=2+,3+} N_{Vi} g S_i \mu_B B_{Si}(\xi) + \chi_0 B \quad (2)$$

$$B_{Si}(\xi) = \frac{2S_i + 1}{2S_i} \coth\left(\frac{2S_i + 1}{2S_i} \xi\right) - \frac{1}{2S_i} \coth\left(\frac{1}{2S_i} \xi\right) \quad (3)$$

$$\xi = \frac{g S_i \mu_B B}{k_B (T - T_0)} \quad (4)$$

Here  $\rho$  is the density of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ , which decreases linearly with the tin content in the alloy from  $8.16 \text{ g/cm}^3$  in  $\text{PbTe}$  to  $6.48 \text{ g/cm}^3$  in  $\text{SnTe}$ ,  $B_{Si}(\xi)$  and  $N_{Vi}$  are the modified Brillouin function and the concentration of the magnetic vanadium ions in  $\text{V}^{2+}(3d^3)$  and  $\text{V}^{3+}(3d^2)$  states with spins  $S=3/2$  and  $S=1$ , respectively. The orbital angular momentum is considered “frozen” and  $g$  factor is equal to 2,  $\chi_0$  is the diamagnetic susceptibility of the host lattice,  $T_0$  is an adjustable parameter that takes into account the exchange interaction of isolated impurity ions,  $\mu_B$  is the Bohr magneton, and  $k_B$  is the Boltzmann constant.

We calculate the theoretical dependences  $M(B)$  and  $M(T)$  by treating concentrations of ions  $N_{V^{3+}}$ ,  $N_{V^{2+}}$ , diamagnetic susceptibility  $\chi_0$  and temperature  $T_0$  as fit parameters. The results of approximation of the experimental field and temperature dependences of the magnetization by the sums of two terms based on the modified Brillouin functions (2)-(4) are shown by solid lines in Figs. 2 and 3. The concentration of vanadium ions in  $\text{V}^{3+}$  and  $\text{V}^{2+}$  states along the investigated  $\text{Pb}_{1-x}\text{Sn}_x\text{V}_y\text{Te}$  ingot determined in this way from the temperature dependences of the magnetization are presented in Fig. 4. Analysis of the obtained results shows that the theoretical and experimental curves virtually coincide for all the samples, and that the data obtained from the field and temperature dependences of the magnetization agree satisfactorily with each other. Diamagnetic susceptibility  $\chi_0$  slightly reduces along the ingot and in the majority of samples  $\chi_0 = -(2.4) \cdot 10^{-7} \text{ emu g}^{-1} \text{Oe}^{-1}$ , which is in good agreement with the theoretical value  $\chi_0 = -3.0 \cdot 10^{-7} \text{ emu g}^{-1} \text{Oe}^{-1}$  for undoped  $\text{PbTe}$  [14]. In the investigated samples, adjustable



**Fig. 4.** Kinetics of changes in concentration of vanadium ions in  $\text{V}^{3+}$  and  $\text{V}^{2+}$  states along the investigated  $\text{Pb}_{1-x}\text{Sn}_x\text{V}_y\text{Te}$  ingot, determined from the temperature dependences of the magnetization.

temperature  $T_0$  varies in the range from  $-0.1$  K to  $0.6$  K. When moving along the ingot, the concentration of  $V^{3+}$  ions increases and then saturates at  $N_{V^{3+max}} \approx 1.7 \cdot 10^{19} \text{ cm}^{-3}$  (see Fig. 4). At the same time, the concentration of  $V^{2+}$  ions increases monotonically from sample 10 to sample 2 up to  $N_{V^{2+}} \approx 2.7 \cdot 10^{19} \text{ cm}^{-3}$ .

It is interesting to note that the total concentration of the magnetic vanadium ions  $N_{V^{3+}} + N_{V^{2+}}$ , which monotonously increases along the ingot, reaches approximately  $4.3 \cdot 10^{19} \text{ cm}^{-3}$ , i.e. only about  $0.3$  mol. % at the end of the ingot (in the sample 2). Moreover, our estimates show that the integral concentration of magnetic vanadium ions in the ingot, dissolving, apparently, in the metal sublattice, is about  $10\%$  of the concentration of vanadium impurities introduced into the crystal ( $y=0.01$ ). This means that most of the impurity introduced into the ingot is in the magnetically neutral state (pushed to the very end of the ingot during growth, forms nonmagnetic microscopic inclusions with tellurium or clusters, etc.).

## 4 Conclusions

The nature of the field and temperature dependences of the magnetization of the investigated  $Pb_{1-x-y}Sn_xV_yTe$  alloys with varying matrix composition and concentration of vanadium impurity, allows us to conclude that the magnetization contains two main contributions: the Brillouin-type paramagnetism of vanadium impurity ions and the diamagnetism of the host crystal lattice. We analyze our experimental results in the framework of the model of electronic structure rearrangement in  $Pb_{1-x-y}Sn_xV_yTe$  alloys upon vanadium doping. An important assumption of this model is that the concentration of  $V^{3+}$  ions in the alloys increases only until the pinning of the Fermi level by the vanadium impurity level lying under the bottom of the conduction band, after which the concentration of  $V^{3+}$  ions saturates and the concentration of  $V^{2+}$  ions starts to increase in its turn.

The experimental field and temperature dependences of the magnetization are successfully approximated by sums of two terms based on the modified Brillouin functions for two different types of impurity ions and temperature-independent contributions, linear in magnetic field. The kinetics of changes in the concentration of magnetic vanadium ions in  $V^{3+}$  and  $V^{2+}$  charge states along the investigated  $Pb_{1-x-y}Sn_xV_yTe$  ingot is determined. It is shown that despite the monotonic increase in the total concentration of the magnetic vanadium ions  $N_{V^{3+}} + N_{V^{2+}}$  along the ingot, it reaches only about  $0.3$  mol. % at the end of the ingot. The integral concentration of magnetic ions of vanadium in the ingot is approximately  $0.1$  mol. %, which is an order of magnitude smaller than the nominal concentration of vanadium introduced in the ingot.

The authors are grateful to M.M. Markina and K.V. Zakharov (M.V. Lomonosov Moscow State University, Faculty of Physics) for assistance in conducting measurements. The work was supported by the Russian Foundation for Basic Research (Project No. 16-02-00865).

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