Solid State Sciences 38 (2014) 30–34

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Unusual paramagnetic centers in PbTe undoped crystals

D.M. Zayachuk [a,*], O.S. Ilyina [a], V.I. Mikityuk [b], V.V. Shlemkevych [b], D. Kaczorowski [c]

[a] Lviv Polytechnic National University, 12 Bandera St, 79013 Lviv, Ukraine
[b] Yuri Fedkovich Chernivtsi National University, 2 Kotsyubynsky St, 58012 Chernivtsi, Ukraine
[c] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 1410, 50-950 Wroclaw 2, Poland

ARTICLE INFO

Article history:
Received 29 August 2014
Accepted 27 September 2014
Available online 30 September 2014

Keywords:
PbTe
Magnetization
Magnetic susceptibility
Native defects
Paramagnetism
Diamagnetism

ABSTRACT

We present the results of the first experimental observation of unusual paramagnetism in solid when magnetic susceptibility of paramagnetic centers doesn't depend on temperature but drastically decreases when the applied magnetic field increases. This unusual combination of the field and temperature dependences of magnetic susceptibility was observed in the studies of magnetization and magnetic susceptibility performed in the wide range of temperatures (1.7–300 K) and magnetic fields (0–5.0 T) on the bulk and surface PbTe powder samples manufactured from crystal ingots grown by Bridgman method out of high-purity Pb and Te. We believe that presence of these features indicate that we are dealing with unknown untypical paramagnetism of paramagnetic centers in solid. We observed that the concentration of such unusual paramagnetic centers in PbTe crystal ingots increases towards their surface. Increase of the concentration of the centers can be so strong that it causes a transition of PbTe from the diamagnetic state to the paramagnetic one in quite wide range of low magnetic fields. Possible nature of the observed unusual paramagnetic centers is discussed.

1. Introduction

Lead and tin chalcogenides are well-known thermoelectric and LED materials. Therefore these semiconductors are constantly in the focus of research [1–3]. Recent research indicated that in these materials properties of bulk and surface layers significantly differ [4,5]. During the growth of crystals with low amount of impurity from melt, entire impurity content might be pushed out onto the surface while the bulk remains undoped [4]. In surface layers of such crystals the low-temperature superconductivity might be observed, while it is absent in the crystal's bulk [5]. Essential differences between surface and bulk properties might have much broader manifestations. In particular, it was shown that a three-dimensional topological insulator doped with magnetic impurities in the bulk can have a regime where the surface is magnetically ordered but the bulk is not [6]. Considering this, we conducted the detailed comparative study of magnetic properties of surface and bulk layers of undoped PbTe crystals, aiming on investigation of defect system and it transformation in the bulk-to-surface transition.

* Corresponding author.
E-mail addresses: zayachuk@polynet.lviv.ua, dzayachuk@yahoo.com (D.M. Zayachuk).

http://dx.doi.org/10.1016/j.solidstatesciences.2014.09.012

2. Samples and experiment

Four samples were investigated, among them one bulk and three surface samples, manufactured from three different ingots grown from the melt by a Bridgman technique. High purity (99.9999%) Pb and Te were used for the growth of ingots, which were afterwards additionally purified. In addition, the purity control of the grown ingots was performed by X-ray fluorescence elemental analysis using the Expert 3L analyser with semiconducting PIN detector on thermoelectric cooling. No foreign impurities were observed in the bulk or on the surface of grown ingots within the sensitivity limit ($\sim 10^{-2}$ at %) of the analyser. The ingots had hole conductivity with typical for PbTe hole concentration of the order of 3×10^{18} cm^{-3}. Since only powder samples could have been manufactured out of surface layers of crystalline ingots, powder samples were used for the study. Magnetic measurements were performed in the temperature range 1.72–300 K and in applied magnetic fields up to 5 T using a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer.

3. Experimental results

Main results are presented in Figs. 1 and 2.

For convenience the investigated temperature range is divided into three regions: medium and high temperature range – between

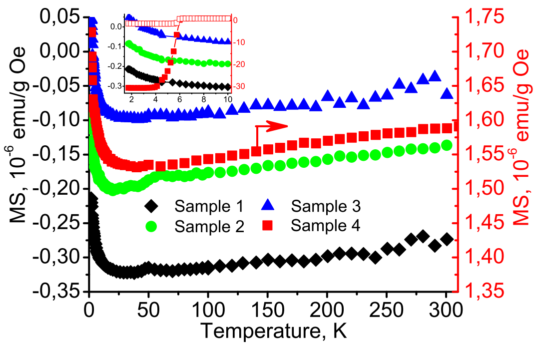

Fig. 1. MS vs. T. Inset: MS vs. T below 10 K for increasing T (solid symbols) and decreasing T (open symbols).

~25÷30 K and room temperature; low temperature range – between ~7 and 25÷30 K; and extra-low temperature range below 7 K.

3.1. *Medium and high temperature range*

Temperature dependences of magnetic susceptibility (MS) χ are identical for bulk and surface samples: MS slowly and monotonously increases with the increase of temperature. MS of the bulk sample (curve 1, Fig. 1) is the lowest. MS of surface samples can be obtained by virtually parallel shift of MS of the bulk sample by a temperature-independent value MC $\Delta\chi$, different for the different samples. At the same time, in the wide range of relatively weak magnetic fields surface samples can even transit to very strong paramagnetic state, like for example Sample 4 (curve 4, Fig. 1). This sample in the following discussion will be called "paramagnetic", although having in mind that it is actually paramagnetic only in certain range of relatively low magnetic fields.

3.2. *Low temperature range*

Cooling to low temperatures fundamentally changes the character of temperature dependence of MS. MS of the samples starts rising quickly with the decrease of temperature, similarly to Curie law for paramagnetics, χ~1/T (Fig. 1).

3.3. *Extra-low temperature range*

Further cooling does not change the character of temperature dependence of MS of diamagnetic samples – it keeps rising. At the same time, some of the samples still remain diamagnetic down to the lowest investigated temperature of 1.7 K (curves 1 and 2, Fig. 1). Other become paramagnetic in the weak magnetic fields (curve 3, Fig. 1). However, behavior of the paramagnetic sample is fundamentally different. At temperatures below ~7 K its MS starts quickly decreasing and the sample transits to strong diamagnetic state, characteristic for a superconductor. In this diamagnetic range temperature dependence of MS χ(T) and field dependence of magnetization M(H) feature well-pronounced hysteresis properties (inset, Figs. 1 and 2).

MS of the investigated samples, unlike that of typical diamagnetics, is not constant at all temperatures but strongly decreases with the increase of magnetic field strength. Experimental dependences χ(H) are close to exponential, especially at high temperatures (inset, Fig. 2).

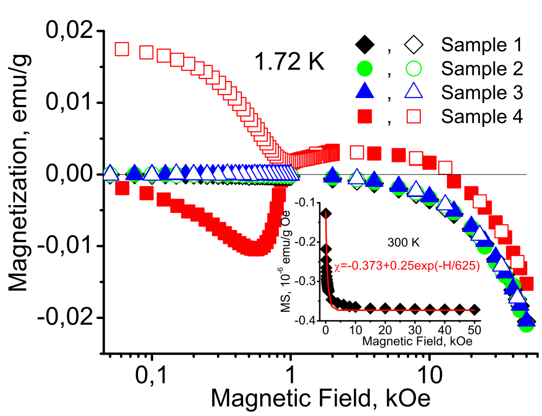

Fig. 2. Magnetization of the investigated samples vs. magnetic field for increasing H (solid symbols) and decreasing H (open symbols). $T = 1.72$ K. Inset: MS for sample 1 vs. magnetic field at 300 K.

4. Discussion

The temperature changes of MS indicate that the investigated PbTe samples contain at least two fundamentally different types of paramagnetic centers. The contribution of one of these is predominant in the medium and high temperature ranges. The characteristic feature of MS of these centers (we call them type I centers) is their independence of temperature. Bulk and surface samples significantly differ in concentration of these centers. The contribution of another type of paramagnetic centers (type II centers) is predominant in low and ultralow temperature ranges. They create the temperature-dependent Curie-like component of the total MS of the samples, χ~1/T.

Type I paramagnetic centers with temperature-independent MS are of special interest. Only one type of temperature-independent paramagnetism is known, namely van Vleck polarization paramagnetism, which emerges when electronic shells of weakly interacting atoms do not have spherical symmetry [7]. At the same time field dependences of magnetization of the investigated samples are not compatible with the standard van Vleck paramagnetism of non-spherical atoms. These incompatibilities are especially evident in the case of the paramagnetic sample 4.

The data presented in Fig. 1 make it evident that in magnetic field of 1000 Oe MS of the sample 4 is colossal – in excess of $+1.5 \times 10^{-6}$ emu g^{-1} Oe^{-1}, even though the crystal lattice of PbTe is diamagnetic and, as will be shown below and is known from literature [8,9], its MS is $-(0.3÷0.45) \times 10^{-6}$ emu g^{-1} Oe^{-1} when $T \to 0$ K. From comparison of these results it follows that in the weak magnetic field paramagnetism of suggested type I centers much exceeds diamagnetism of crystal lattice. If type I centers' paramagnetic susceptibility was independent of magnetic field, as would be the case for van Vleck's polarization-paramagnetism, then their paramagnetism would exceed the diamagnetism of crystal lattice in any magnetic field, and sample's magnetization would increase with the increase of applied magnetic field. Experiment shows the opposite – in the range of high magnetic fields magnetization of the sample 4 decreases with the increase of magnetic field and the sample transits to diamagnetic state. Therefore, in high magnetic fields diamagnetic susceptibility of crystal lattice exceeds paramagnetic susceptibility of the type I centers. Since MS of crystal lattice is independent of magnetic field, this indicates that increase of magnetic field leads to the decrease of paramagnetic susceptibility of such centers. Thus we conclude that in the investigated samples we observe untypical behavior of paramagnetic centers in solid, whose paramagnetic susceptibility is temperature-independent but decreases with the increase of applied magnetic field.

As was mentioned earlier, experimental dependences χ(H) of investigated samples are close to exponential. Such behavior cannot be caused by neither diamagnetic matrix nor typical