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Small Eu Complexes into the Bulk and the Surface Layers of PbTe:Eu Crystals Doped With Different Impurity Concentration

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We present the results of the first experimental evidence of inverse distribution of small magnetic complexes of Eu impurity along the bulk axis and the lateral surfaces of the PbTe:Eu crystal ingots grown from doped melts with significantly different initial concentrations of doping impurity $N_{int}(Eu)$ in the melt. If the Eu concentration is high enough, that the doping impurity enters into the bulk of doped ingot during the process of its growth ($N_{int}(Eu) = 1\cdot10^{20}$ cm^{-3}), the mainly small complexes of Eu are formed in the beginning of the ingot and probability of their formation decreases towards the end of ingot. If the Eu concentration is low enough, that the doping impurity is pushed out onto the surface of doped ingot during its growth ($N_{int}(Eu) = 1\cdot10^{19}$ cm-3), probability of the complex formation is minimal in the beginning of ingot and increases towards the ingot's end. An eventual role of the background impurity of Oxygen in formation of the revealed peculiarities of Eu doping impurity distributions in PbTe:Eu crystals is discussed.

Key words: IV-VI semiconductors, crystals, impurities, doping, rare earth elements, magnetization, magnetic susceptibility

Introduction

For a long time rare earth elements (REE) have been successfully used in controlling quality and other physical parameters of semiconductors, especially of IV-VI ones. Since the REE impurities have got uncompensated spin moments of the inner $4f$ electrons, their behavior can be effectively studied by examining the magnetization and magnetic susceptibility (*MS*) of the doped samples. Since the magnetization and MS are sensitive to the state of the magnetic impurity, they provide useful information about the various magnetic interactions in the doped crystal. In particular, such studies have shown that the magnetic properties of *PbTe:Eu* doped crystals are to large extent determined by the complexes of *Eu* with the background Oxygen impurity in the crystal matrix of the doped lead telluride [1]. High sensitivity of magnetization and MS of doped crystals to the state of magnetic impurities has been used in the presented study to obtain information about the formation of different magnetic centers in *PbTe:Eu* crystals grown from melts with different concentrations of impurities.

Our recent studies [2, 3] showed that the initial value of impurity concentration in the melt for growing of *PbTe:Eu* crystals determines the behavior of impurity during the solidification of the doped melt. If this concentration is sufficiently high, approximately $1\cdot10^{20}$ cm^{-3}, the doping impurity enters into the bulk of doped crystals and concentrates in the initial part of the ingot spanning about 2/3 of its length. If $N_{int}(Eu)$ is lower, about $1\cdot10^{19}$ cm^{-3} and less, the doping *Eu* impurity is pushed out onto the surface of doped ingot and is distributed along the lateral surface of the entire length of ingot. It was suggested that the decisive role in this behavior of *Eu* impurity in the process of growing of *PbTe:Eu* doped crystals from melt belongs to uncontrolled impurity of Oxygen. This work is devoted to the search for additional independent evidence to support this hypothesis by studying the magnetic properties of bulk and surface of *PbTe:Eu* crystals, grown from melts with different initial concentration of doping impurity.

I. Growth and characterization of ingots

The doped *PbTe:Eu* crystal ingots were grown from
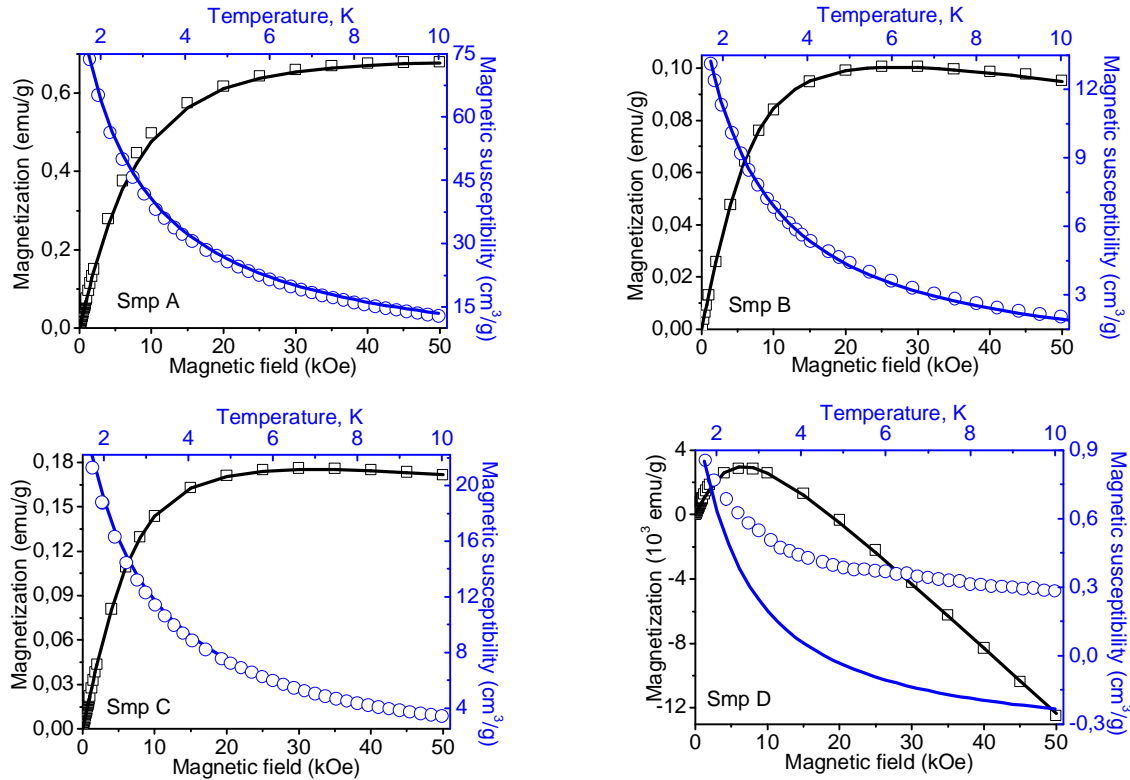
Fig. 1. Magnetization vs. magnetic field (T = 1.72 K) and *MS* vs. *T* of investigated samples (for designations and calculation parameters refer to Table 1). The symbols are the experimental data; the solid lines are the results of calculations.

melt by the Bridgman method and doped with *Eu* in the process of growth. The crystal ingots have a conical-cylindrical shape. The ingot length was approximately 30 mm, the diameter of their cylindrical part 10 mm, the ratio between lengths of the cylindrical and conical parts of ingots about 2:1. Two different initial concentrations of *Eu* impurity $N_{int}(Eu)$ in the melts were used, namely $1 \cdot 10^{20}$ and $1 \cdot 10^{19}$ cm^{-3}. The preliminary characterization of the *Eu* impurity distribution in the ingots was performed with X-ray fluorescent elemental analysis and Secondary Neutral Mass Spectroscopy methods. Subsequently four samples were prepared for detailed investigation. Two of them were prepared from the incipient conic parts of ingots approximately 3 mm of length. The third sample was prepared from surface layers of the end parts of ingot doped with *Eu* with $N_{int}(Eu) = 1 \cdot 10^{19}$ cm^{-3}. These were the powder samples. The fourth sample was prepared from the t part of ingot with $N_{int}(Eu) = 1 \cdot 10^{20}$ cm^{-3} in which the volume concentration of *Eu* drastically starts tending to zero. This was the crystal sample. Magnetization and MS of these samples were investigated using a commercial SQUID magnetometer.

II. Experimental results and discussion

The results of experimental investigations of both the field dependences of magnetization *M* at the temperature 1.72 K and temperature dependences of MS at the magnetic field $H = 0.3$ kOe and their quantitative treatment are shown in Fig. 1.

Total magnetization of the doped samples in the magnetic field H was calculated as:

$$M = M_S + M_{P1} + M_{P2} + c_{Matrix} H \qquad (1),$$

where M_S, M_{P1}, M_{P2} are the contributions of the single centers, the nearest-neighbors (NN) with ferromagnetic interaction, and next-nearest-neighbors (NNN) pairs with antiferromagnetic interaction, respectively, and c_{Matrix} is the MS of the crystal matrix under condition T→0 K. For calculation of M_S, M_{P1}, and M_{P2} the standard procedure and standard ratios [4, 5] were used. The values of the exchange integrals between *Eu* ions were taken as $J_1/k_B = 0.056$ K (NN pairs) and $J_2/k_B = - 0.13$ K (NNN pairs) [1]. The concentration of *Eu* as a constituent part of different impurity centers (singles or pairs) and the value of c_{Matrix} are considered as adjustable parameters of calculations. The values of parameters used to reproduce the experimental dependences of *M*(H) and *MS*(T) of the investigated samples, shown in Fig. 1, are presented in Table 1.

There are two the most important results of analytical treatment of obtained experimental data.

The first of them is that distributions of *Eu* single centers and the smallest Eu-Oxygen complexes are opposite for the cases when doping impurity enters into the bulk of doped ingot ($N_{int}(Eu) = 1 \cdot 10^{20}$ cm^{-3}) or is pushed out onto the ingot's surface ($N_{int}(Eu) = 1 \cdot 10^{19}$ cm^{-3}). In the first case the small complexes (*NN* and *NNN* pairs) dominate in the beginning of doped ingot. Towards the ingot's end the concentration of pairs decreases and

The investigated samples and the values of the corresponding parameters used for calculation of the dependences of $M(H)$ and $MS(T)$, shown in Fig. 1.

The sample	$N_{int}(Eu)$, cm^{-3}	Position in ingot	N_{Eu} (Single), cm^{-3}	N_{Eu} (NN pairs), cm^{-3}	N_{Eu} (NNN pairs), cm^{-3}	χ_{Matrix}, 10^{-6} cm^3/g
A	$1 \cdot 10^{20}$	Beginning	$2.14 \cdot 10^{19}$	$3.72 \cdot 10^{19}$	$2.71 \cdot 10^{19}$	+0.15
B	$1 \cdot 10^{20}$	~1/3 length from ending	$1.47 \cdot 10^{19}$	0	0	−0.41
C	$1 \cdot 10^{19}$	Beginning	$2.46 \cdot 10^{19}$	0	0	−0.41
D	$1 \cdot 10^{19}$	Ending	0	$1.04 \cdot 10^{18}$	0	−0.41

the *Eu* single centers become dominating (The samples A and B, Table 1). At that both the dependencies $M(H)$ and $MS(T)$ for samples from beginning and ending of the doped part of ingot can be described very well by the same set of parameters (Fig. 1). However, the lattice magnetic susceptibility χ_{Matrix} is very different for these samples. It's positive in the beginning of ingot where the small complexes dominate (The sample A) and negative in the middle part of the ingot where the *Eu* single centers dominate (The sample B). These results confirm our previous data [1, 6] and are consistent with suggestions presented there about the mechanism of formation of the positive magnetic susceptibility of the *PbTe* crystal lattice. In the second case, on the other hand, in the beginning of doped ingot the *Eu* single centers dominate (The sample C) whereas in the end of doped ingot on its surface only the small *NN* complexes of *Eu* are observed (The sample D).

Apparently, it is exactly the revealed differences in formation of the *Eu* complexes what determines the differences in *Eu* distribution along the axis and surface of doped ingot, when the impurities enters into the bulk of doped ingot or pushed out onto its surface observed in [2]. As was mentioned before the small complexes of *Eu* in the doped *PbTe:Eu* crystals are the complexes of Europium with the background Oxygen impurity [1]. In the process of growth of the *PbTe:Eu* crystal from the doped melt these complexes can be formed at the solid – liquid interface in front of the crystallization front and behave like impurities with segregation coefficient less than one being pushed into the liquid phase [2]. Since the radial redistribution of Eu in the surface layers occurs under strongly non-equilibrium conditions due to rapid heat removal through lateral surfaces. For this reason decay of the complexes in the liquid phase is not efficient enough and they are pushed to the end of the ingot along the doped surface. So in the beginning of the doped ingot grown from the melt with a low initial concentration of *Eu* the single impurity centers are prevalent and in the end of ingot the small *Eu* complexes on its surface are predominant.

The second important result is that it is not possible to quantitatively describe both dependences $M(H)$ and $MS(T)$ with the same value of parameter χ_{Matrix} for the sample prepared from surface layers of the end of the doped ingot with $N_{int}(Eu) = 1 \cdot 10^{19}$ cm^{-3} (The sample D, Fig. 1). Moreover, the dependence of $MS(T)$ under the investigated temperature range, in contrast to all other

samples, cannot be described by the ratio (1) for any fixed value of χ_{Matrix}. A similar behavior of MS of the surface layers of doped *PbTe:Eu* ingots was observed by us earlier and it was explained by the existence of superconducting Pb-based inclusions [7]. It appears that here we see the manifestation of the same effect.

Conclusions

Magnetization and magnetic susceptibility of the bulk and surface samples of *PbTe:Eu*-doped crystals grown by the Bridgman method from the melts with two different initial concentrations of *Eu* impurity $N_{int}(Eu) = 1 \cdot 10^{19}$ and $1 \cdot 10^{20}$ cm^{-3} are investigated. The relative contributions to the magnetic properties of the Eu single centers, the nearest-neighbors (NN) and next-nearest-neighbors (NNN) pairs within Europium and Oxygen complexes are determined. The dependence of consistent pattern of distribution of the small Eu complexes on the initial concentration of doping impurity in the melt was revealed. It is shown that these distributions are inverse for the low and high initial impurity concentration $N_{int}(Eu)$. For the high initial impurity concentration $N_{int}(Eu) = 1 \cdot 10^{20}$ cm^{-3}, when the doping impurity enters into the bulk of doped crystal the probability of pair formation is maximal in the beginning of ingot and decreases towards its end. Vice versa, if the initial impurity concentration is low $N_{int}(Eu) = 1 \cdot 10^{19}$ cm^{-3} and the doping impurity is pushed out onto the surface of doped ingot, the probability of pair formation is minimal in the beginning of ingot and increases towards its end. We consider these data as the independent evidence to support our previous suggestion [2] that the uncontrolled background impurity of Oxygen plays an decisive role in the behavior of Eu impurity during the process of PbTe:Eu crystals growth from the doped melts.

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Дрібні комплекси *Eu* в об'ємі та поверхневих шарах кристалів *PbTe*:*Eu* легованих різною концентрацією домішки

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Представлено результати перших експериментальних доказів діаметрально протилежного розподілу дрібних магнітних комплексів домішки *Eu* вздовж об'єму та бокових поверхонь кристалічних зливків *PbTe:Eu*, вирощених з легованих розплавів з істотно різною початковою концентрацією легуючої домішки $N_{int}(Eu)$. Якщо концентрація *Eu* досить висока, така, що в процесі росту легуюча домішка входить в об'єм легованого зливку ($N_{int}(Eu) = 1\cdot10^{20}$см$^{-3}$), то дрібні комплекси *Eu* формуються в основному на початку зливку, а в напрямку до його кінця ймовірність формування комплексів зменшується. Якщо концентрація домішки *Eu* настільки мала, що вся вона в процесі росту виштовхується на поверхню легованого зливку ($N_{int}(Eu) = 1\cdot10^{19}$см$^{-3}$), ймовірність утворення комплексів мінімальна на початку зливку і збільшується у напрямку до його кінця. Обговорюється можлива роль фонової домішки Кисню у формуванні виявлених особливостей розподілу домішки *Eu* в кристалах *PbTe: Eu*.

Ключові слова: напівпровідники $A^{IV}B^{VI}$, кристали, домішки, легування, рідкісноземельні елементи, намагніченість, магнітна сприйнятливість.