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States of paramagnetic impurities and laser-induced decomposition of impurity clusters in lead telluride

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Abstract. Electrical and optical properties as well as the EPR of PbTe:Eu single crystals before and after an IR laser emission treatment in the matrix transparency region have been studied. Parameters of the spin Hamiltonian for Eu^{2+} ions in PbTe have been determined. It has been established that the IR laser treatment has a considerable effect on PbTe:Eu characteristics, allowing properties of the crystals to be changed over a wide range. Thus, a change-over in the conductivity type of the crystals from the p type ($P_{77\text{K}} = 4 \times 10^{18} \text{ cm}^{-3}$) to the n type (up to $N_{77\text{K}} = 1 \times 10^{19} \text{ cm}^{-3}$) was attainable. The application of the IR laser emission made it possible to reveal a HFS in EPR spectra of Eu^{2+} ions and to separate the lines corresponding to Eu isotopes ^{151}Eu and ^{153}Eu . The changes in the electrical characteristics and EPR spectra of the crystals investigated are attributed to decomposition under the action of the IR laser radiation of Eu-enriched complexes.

1. Introduction

The problem of impurity and defect states in IV–VI semiconductors and especially in lead telluride (PbTe), which has been studied to the greatest extent, appears to be at present most important from the standpoint of a practical application of these materials. A great variety of experimental data on the effect that doping with various impurities has on the properties of PbTe [1] made it possible to ascertain that most of the impurity states can be explained in the model of localised states. These states can be treated as ‘deep states’ both in the band gap and in the conduction or valence bands. The studies of electrical, optical, magnetic and other properties, however, in the overwhelming majority of cases failed to make it possible to ascertain the charge states of the impurity centres. However, these are important both from an applied standpoint for determining the mechanisms of recombination of non-equilibrium carriers and from a scientific viewpoint for establishing the spectrum of impurity states and its relation to the band spectrum, the effect of the environment, etc.

IV–VI semiconductors exhibit a low thermodynamic stability [2] and, as a consequence, a broad region of homogeneity, because of relatively low enthalpies of formation of metal and chalcogen vacancies ($\Delta H \approx 0.5 + 0.7 \text{ eV}$) [3]. In these semiconductors the vacancies are electrically active. The introduction of impurities most probably results in the formation of crystalline structure fragments [4] because of lower (as a rule) enthalpies of formation of ‘impurity–Te’ bonds. In addition, metal- and Te-enriched electroneutral inclusions arise owing to, for example, a concentrational supercooling [5]. A substantial

change in properties is therefore possible under the action of external factors breaking down such fragments or inclusions, which was demonstrated, e.g. in [6], on irradiation of these semiconductors with an IR laser emission of a relatively low power density ($W \approx 40 \text{ W cm}^{-2}$) in the matrix transparency region $\hbar\omega < E_g$, where E_g is the band gap.

To establish the charge state of impurity centres, their complexing, the effect of the environment, and the time history of changes in the properties of IV–VI semiconductors under the action of external effects, it is expedient to use EPR-active impurities.

The Mn impurity, which has been rather well studied in PbTe (for references see, e.g., [7]) and which is in the Mn^{2+} state, is generally used as such EPR-active centre. The constants of a superhyperfine interaction of Mn with ^{127}Te and ^{125}Te have been recently determined for PbTe layers ion implanted with Mn [7]. The Eu impurity (being presumably in the Eu^{2+} state [8]) was chosen for our experiments. While the EPR of Mn^{2+} in the PbTe lattice has been well studied, no data on the EPR behaviour of Eu^{2+} ions in PbTe nor on the spin-Hamiltonian (SH) constants are available to our knowledge.

Main emphasis in the study was placed on investigating the effect of Eu on the properties of PbTe and the EPR spectra of Eu ions in PbTe with the aim of ascertaining the state of Eu ions and determining its position in the lattice as well as examining the effect of IR laser emission on the behaviour of Eu in the PbTe lattice.

2. Samples and their electrical characteristics

The PbTe:Eu single crystals (NaCl-type lattice) were grown by the Czochralski method. The impurity content in the melt was 0.02–0.2 mass %. The Eu impurity was introduced into the melt as the EuS compound. The introduced sulphur was assumed not to affect the PbTe properties significantly as it is an isoelectronic impurity. The crystals had a p-type conductivity with a hole concentration $P_{77\text{K}}$ at liquid-N temperature of $(2\text{--}5) \times 10^{18} \text{ cm}^{-3}$ regardless of the impurity concentration. Undoped PbTe crystals grown by this method had the same hole concentration.

According to the electrophysical properties, the PbTe:Eu crystals could be divided into two groups. For crystals in the first group, with the lowest Eu concentration, the temperature dependences of the Hall coefficient $R_H(T)$ did not differ from similar dependences for undoped crystals and the carrier mobility in these samples μ_p was about $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T = 77 \text{ K}$. Single crystals in the second group, with an impurity content $N_{\text{Eu}} > 0.02 \text{ mass } \%$, exhibited a considerably lower free-hole mobility in the region of $T = 77 \text{ K}$ compared with those of undoped crystals or crystals with the lowest Eu content. The $R_H(T)$ dependences featured anomalies in temperature region $T = 4.2\text{--}100 \text{ K}$ (figure 1, curve A), which can presumably be attributed to the formation of Eu-enriched complexes that leads to potential barriers at the inclusion–PbTe matrix interface. This was corroborated by high photo-EMF signals in the absence of a bias, which were detected in these samples at a temperature below 100 K, and by the emergence of a potential relief by the electron-beam-induced current method.

Next, the samples at $T = 300 \text{ K}$ were subjected to the emission from an IR CW CO_2 laser (model ILGN-704) with a photon energy $\hbar\omega$ of 0.118 eV in the matrix transparency region $\hbar\omega < E_g$ (where $E_g(300 \text{ K}) = 0.32 \text{ eV}$ is the PbTe band gap).

After the laser treatment the PbTe:Eu crystals with an impurity concentration of 0.02 mass % exhibited a decrease in the hole concentration to $P_{77\text{K}} \approx 10^{17} \text{ cm}^{-3}$. The time rate of the concentration change at a fixed emission power density did not differ from the rate of the carrier concentration change in undoped p-PbTe samples. The

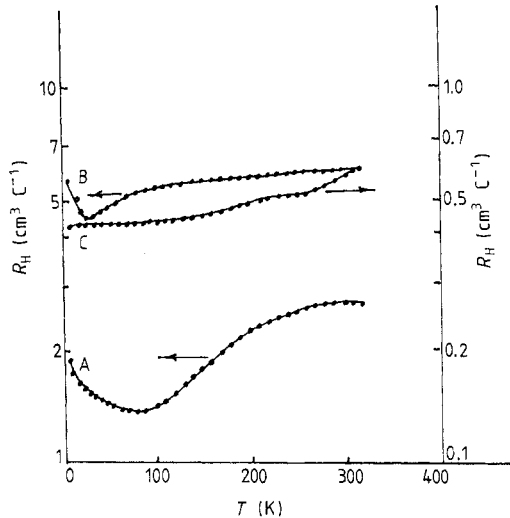


Figure 1. Temperature dependences of the Hall coefficient in a single-crystal PbTe:Eu sample ($N_{\text{Eu}} = 0.2$ mass %) (laser emission power density $W = 20 \text{ W cm}^{-2}$): curve A, before processing with IR laser emission; curve B, irradiation time of 4.5 h (p type); curve C, irradiation time of 10 h (n type).

mechanism of the free-carrier concentration changes under the action of IR laser emission in the crystal transparency region was discussed in [9]. Under the combined action of laser emission and an external electric field on the rate of concentration change in PbTe:Eu single crystals increased by a factor of 10. Also it was possible to change the sample conductivity type from p type to n type and to obtain crystals with an electron concentration $N_{77\text{K}}$ of up to $1 \times 10^{19} \text{ cm}^{-3}$.

Considerable changes occurred in the $R_{\text{H}}(T)$ dependences for crystals subjected to the IR laser treatment. The initial dependence (figure 1, curve A) was transformed to that presented in curve B. The changes observed are attributed to dissociation of Eu-enriched complexes under the action of the laser treatment. Owing to the emergence of potential barriers in initial unirradiated crystals in the temperature range $T = 4.2\text{--}100 \text{ K}$, the free-carrier scattering mechanism changes compared with that for undoped crystals, and a 'parasitic' EMF arises at the matrix-inclusion interfaces, which gives rise to an anomaly in the $R_{\text{H}}(T)$ dependence. The laser emission causes decomposition of the Eu-enriched inclusions and, as a consequence, a decrease in the magnitude of the potential barriers compared with the kT value. Because of this, the distinguishing feature in $R_{\text{H}}(T)$ manifests itself at lower temperatures (figure 1, curve B). After inversion of the conductivity type of the samples from p type to n type, the anomaly in $R_{\text{H}}(T)$ disappears (figure 1, curve C).

Studying the spectral dependences of the optical absorption on the crystals in question demonstrated an increase in the optical transmission of samples with increasing laser exposure dose, from 1–2% for unirradiated samples to 15–20% for samples subjected to the action of the laser emission. This effect is associated with a decrease in the hole concentration and, as a consequence, a decrease in the absorption of free carriers. The absorption coefficient spectral dependences for PbTe:Eu single crystals are very similar to those obtained for stoichiometric undoped PbTe samples with the same free-carrier

concentration. No additional absorption bands associated with the introduced Eu impurity were detected in the spectral range $\lambda = 5\text{--}15 \mu\text{m}$.

3. EPR spectra and discussion of results

EPR studies were conducted on a Varian E-12 spectrometer in the temperature range 4.2–300 K. EPR spectra of initial single-crystal PbTe:Eu samples with the magnetic field direction along the $\langle 100 \rangle$ axis of the PbTe:Eu crystals contain seven partly overlapping lines corresponding to the charge state Eu^{2+} (fine structure $S = \frac{7}{2}$), on a background in which the hyperfine structure (HFS) lines show up weakly (figure 2, spectrum A).

Irradiation of PbTe:Eu samples for several hours with IR emission from a CO_2 laser ($\hbar\omega = 0.118 \text{ eV}$) resulted in a considerable increase in the intensity of the HFS lines (figure 2, spectra B–D). The best resolution of the HFS was attained for the most intense central line of the spectrum, which belongs to the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ transition (the transitions between Eu^{2+} states are shown in figures 2 and 3). The greater the distance from the spectrum centre, the lower is the intensity of the structure lines and the less resolved the HFS becomes.

The angular dependence of the EPR spectrum on rotation of the magnetic field in the (001) plane was investigated for single-crystal samples irradiated with the IR emission, which the best HFS resolution had been obtained (figure 3). For the magnetic field direction along $\langle 100 \rangle$ ($\theta = 0^\circ$), fine structure lines are maximally spaced over the field. As the magnetic field is rotated, the spectrum ‘convolutes’ into a single line ($\theta = 31^\circ$) and then expands again ($\theta = 45^\circ$). The trend of the angular dependence of the spectrum in the segment $90^\circ\text{--}45^\circ$ is mirror symmetrical to the trend in the segment $0\text{--}45^\circ$. Thus the angular dependence of the EPR spectrum corresponds to cubic symmetry of the centre.

PbTe has a NaCl-type structure (point symmetry, O_h). For point symmetry O_h the SH at spin $S = \frac{7}{2}$ has the form [10]

$$\mathcal{H} = g\beta\hat{H} \cdot \hat{S} + b_4\hat{O}_4 + b_6\hat{O}_6 + A\hat{S} \cdot \hat{I} \quad (1)$$

where the term $g\beta\hat{H} \cdot \hat{S}$ is the Zeeman splitting, $\beta = e\hbar/2m_0c$, S is the electron spin and I is the nucleus spin. The last term describes the isotropic Fermi contact hyperfine interaction of ^{151}Eu ($I = \frac{5}{2}$) and ^{153}Eu ($I = \frac{5}{2}$). $b_4 = 60B_4$ and $b_6 = 1260B_6$ [10] are the cubic field splitting parameters, and \hat{O}_n are the spin operators.

The basic term of the ion $\text{Eu}^{2+} \ ^8\text{S}_{7/2}$ (electronic configuration $4f^7$) in a cubic field is split into two doublets Γ_6 and Γ_7 and a quartet Γ_8 . Depending on the sign and value of constants b_4 and b_6 , either the doublet Γ_6 or the doublet Γ_7 may be lower. For ions in the S state the splitting in a cubic crystalline field is obtained for high orders of the perturbation theory.

Obtaining the SH (equation (1)) energy levels at an arbitrary magnitude and orientation of the magnetic field requires diagonalisation of the 8×8 matrix. For some cases, such as $\mathbf{H} \parallel \langle 100 \rangle$, the SH (equation (1)) energy levels have been obtained in an analytical form [11].

The observed EPR spectra are described sufficiently well for a strong magnetic field by a spectrum with transitions at frequencies

$$\begin{aligned} +\frac{1}{2} \leftrightarrow -\frac{1}{2} & \quad \hbar\omega = g\beta H_0 \\ \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2} & \quad \hbar\omega = g\beta H_0 \mp 12pb_4 \pm 14qb_6 \end{aligned}$$

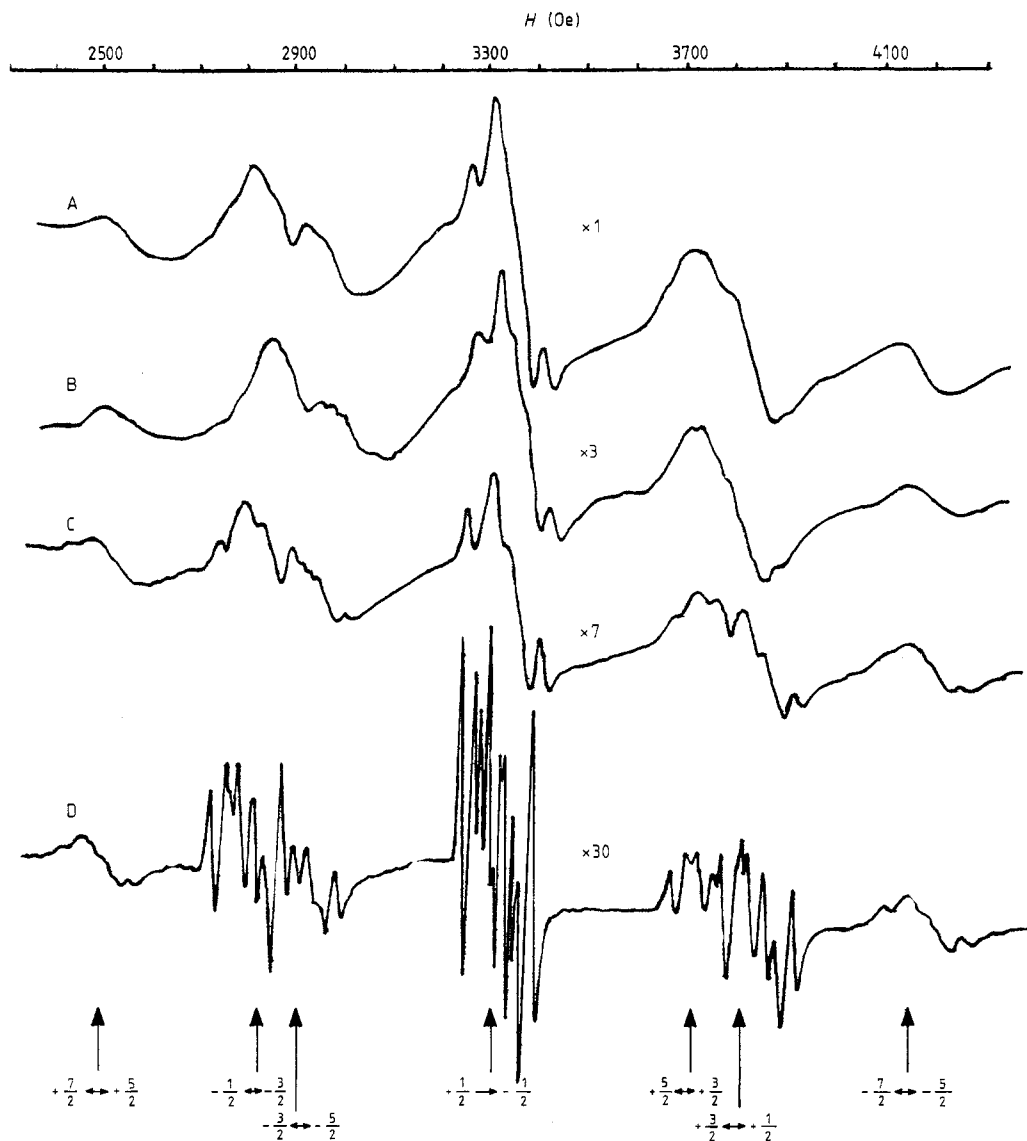


Figure 2. EPR spectra of Eu^{2+} in PbTe with the magnetic field direction along the $\langle 100 \rangle$ axis of PbTe ($W = 20 \text{ W cm}^{-2}$): spectrum A, $P_{77\text{K}} = 4.09 \times 10^{18} \text{ cm}^{-3}$, before irradiation; spectrum B, EPR spectrum after irradiation for 1 h; spectrum C, EPR spectrum after irradiation for 2 h; spectrum D, EPR spectrum after irradiation for 4 h ($P_{77\text{K}} = 3.63 \times 10^{17} \text{ cm}^{-3}$). The factors on the central lines of spectra indicate how many times its intensity increased after the action of IR laser emission.

$$\pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2} \quad \hbar\omega = g\beta H_0 \mp 10pb_4 \mp 14qb_6$$

$$\pm \frac{7}{2} \leftrightarrow \pm \frac{5}{2} \quad \hbar\omega = g\beta H_0 \pm 20pb_4 \pm 6qb_6$$

where $p = 1 - 5\varphi$; $\varphi = l^2m^2 + m^2n^2 + l^2n^2$; $q = \frac{3}{2}(11l^2m^2n^2 - \varphi + \frac{2}{3})$; l, m, n are direction cosines between H_0 and the cubic axes.

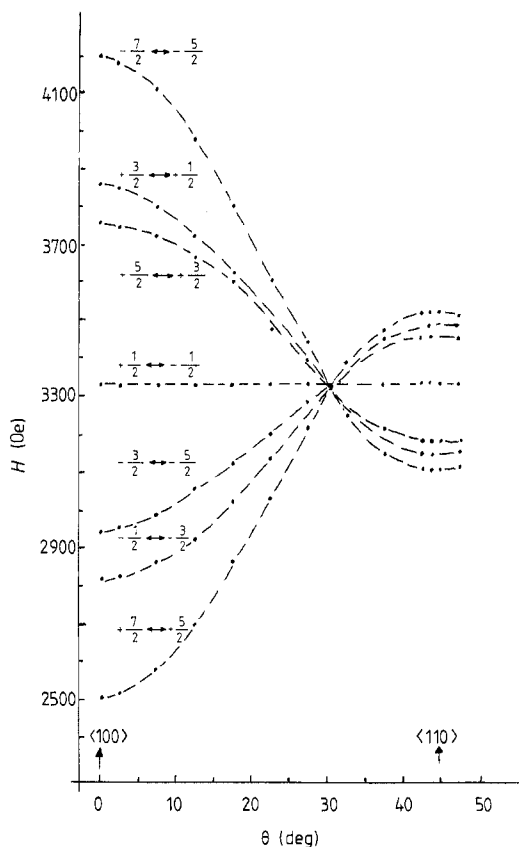


Figure 3. Angular dependence of the fine structure of EPR of Eu^{2+} ions in PbTe (for the sample in figure 2, curve C). The magnetic field direction changes from $[100] \rightarrow [110] \rightarrow [010]$ in the (001) plane.

Studies of the temperature dependences of the intensities of the EPR lines of PbTe:Eu crystals with a pronounced HFS made it possible to ascertain the order of arrangement of the levels and to determine the signs of the SH constants. From an analysis of the experimental results obtained, all the lines in the spectrum were identified and the HFS lines belonging to the Eu isotopes ^{151}Eu and ^{153}Eu were determined. The SH (equation (1)) constants are as follows: $g = 1.9975 \pm 0.0005$; $b_4 = + (40.1 \pm 0.45) \times 10^{-4} \text{ cm}^{-1}$; $b_6 = - (0.63 \pm 0.45) \times 10^{-4} \text{ cm}^{-1}$; $A = (26.1 \pm 0.45) \times 10^{-4} \text{ cm}^{-1}$ (^{151}Eu); $A = (11.8 \pm 0.45) \times 10^{-4} \text{ cm}^{-1}$ (^{153}Eu). The ratio $A_{^{151}\text{Eu}}/A_{^{153}\text{Eu}}$ of the HFS constants obtained from these experiments is equal to the ratio of the nuclear magnetic moments of the isotopes.

The presence of seven broad lines in the EPR spectra of PbTe:Eu crystals not irradiated with an IR laser, the considerable increase in the intensity of the EPR lines (the maximum recorded increases in the EPR line intensity exceeded two orders of magnitude) and the appearance of well resolved HFS spectra provide evidence that clustering of the impurity Eu or the appearance of Eu-enriched complexes occurs during the growth of these crystals. The lines of the EPR spectrum of unirradiated crystals are broadened, and the HFS of solitary ions Eu^{2+} stemming from the interaction

of 4f electrons with the spin of its own nucleus shows up weakly in the background of the lines. Such a clustering is also characteristic of another paramagnetic impurity, Mn, in the lattice; the formation of Mn-enhanced inclusions is promoted at high temperatures ($T > 340^\circ\text{C}$) [7]. IR laser irradiation of the crystals in the matrix transparency region causes the dissociation of such complexes owing to existence of a considerable grad T between inclusions (enriched in metallic components) and the semiconductor matrix [9], with the result that Eu^{2+} ions diffuse into points of the metallic sublattice of PbTe. The Eu impurities in inclusions appear to be in an electrically neutral state and are not EPR active. When the Eu^{2+} ions diffuse into metallic sublattice points, they compensate for two holes of each Pb vacancy, causing a decrease in the free-hole concentration or leading to inversion of the conductivity type of PbTe:Eu crystals (see § 2), which is due to the existence of Te vacancies, each of which is a doubly charged donor. The diffusion of Eu impurities from inclusions into metallic sublattice points results in a considerable increase in the intensity of the EPR spectra and the appearance of a well resolved HFS of the spectra from the two Eu isotopes ^{151}Eu and ^{153}Eu , which are in a solitary state in the cubic field of the crystal.

4. Conclusion

Electrical and optical properties as well as the EPR of PbTe single crystals doped with Eu impurities and subjected to IR laser emission treatment in the matrix transparency region have been studied. The SH constants for Eu^{2+} ions in the PbTe matrix have been determined. It has been shown that the IR laser irradiation has a considerable effect on the physical properties of PbTe:Eu, which allows the crystal properties and EPR spectra to be changed over a wide range. The application of IR laser irradiation seems to enable a high degree of perfection of crystal properties to be attained by breaking down the complexes enriched in paramagnetic impurities during the laser treatment. This manifests itself, for example, in a considerable increase in the intensity of the EPR signals and the presence of HFS lines in the spectra, which allowed the SH parameters of Eu^{2+} ions in the PbTe matrix to be determined.

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