Lanthanide doping of $\text{A}^{\text{III}}\text{B}^{\text{V}}$ crystals

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Abstract. The state of rare earth impurities at concentrations of about $10^{18}$ cm$^{-3}$ in volume-doped $\text{A}^{\text{III}}\text{B}^{\text{V}}$ semiconductor crystals can be described in the framework of the model of quasi-molecular rare earth centers of Ln$_2$O$_3$ type and spontaneous polarization regions-coupled spin-polarons localized on small donors.

1. Introduction

The interest in lanthanides as an alloying admixture of semiconductor crystals is due to their bright physical and chemical properties. For example, some studies have shown that due to the high chemical activity of rare earth elements, it is possible to form metal clusters in Germany and silicon, which are clusters that serve as effective effluents for radiation defects [1, 2]. In addition, the introduction of rare earth impurities can be used to "purify" crystals by binding uncontrolled impurities. However, this does not exhaust the possibility of using rare earth impurities in crystal alloying. Apparently, no less interesting is the possibility of using lanthanides to create new optical materials based on semiconductors doped with rare earths, which are characterized by unique properties due to the structure of the electron shell of rare earth atoms.

Due to the high chemical activity of the elements of the lanthanide group, the question of the state of atoms of rare earth elements introduced into semiconductor crystals and their distribution over the crystal is relevant.

The electrical and optical properties of semiconductor materials, due to impurity and intrinsic defects and of greatest interest in the creation of solid-state electronics devices, are inextricably linked to their magnetic properties. The latter are most adequately reflected in the behavior of the magnetic moment, which can be reliably controlled by the temperature dependences of the magnetization of the studied samples.

In this article, we discuss the behavior of rare earth impurities in volume-doped $\text{A}^{\text{III}}\text{B}^{\text{V}}$ crystals grown by the Chochralski, Bridgeman, and solution-melt methods. Alloying occurred during the growing process by introducing a rare earth metal into the melt. The concentration of the introduced impurity was about $10^{18}$ cm$^{-3}$ and was controlled by spectral and neutron activation analysis [3].
2. Materials and methods
Measurements of temperature dependences of magnetization in the temperature range from 3.2 to 300 K at the intensity of the external magnetic field up to 15 ke were carried out by the Faraday method on a special installation, which was created on the basis of the spectrometer MGD 312 FG. The samples were placed in an external magnetic field in a quartz Cup suspended from a thin quartz thread. Registration of intensity of interaction with a magnetic field was made in conditions when the sample reached a state of thermodynamic equilibrium. Control of this state was carried out by means of the automated control system of measurements with the specially developed software. Calibration of the installation was carried out using a reference sample, which was used as a single crystal of magnetically pure indium phosphide with a susceptibility of $\chi = -313 \cdot 10^{-9}$ cm$^3$/g. The mass of the sample was determined on the scales BP 211 D with an accuracy of $10^{-5}$ g [1].

3. Results and discussion
Studies of rare-earth impurity states carried out in [4,5] showed the fundamental possibility of the formation of substitutional solid solutions with single lanthanides statistically distributed over the crystal in the Ln (III) charge state. However, the success was very limited – the total number of lanthanides has managed to register the EPR spectra of only two lands – ytterbium and gadolinium. In addition, the erbium spectrum on crystals doped by ion implantation was observed in [6], which was interpreted as tetrahedral with weak axial distortion.

All attempts to detect single impurity centers of other rare earth elements from studies of EPR spectra and temperature dependences of magnetization have not been successful.

The most obvious explanation of the obtained results of the research, apparently, is a significant excess of the ionic radii of lanthanide atoms of the radius of the substituted cation [7]. The known effect of lanthanide compression [7] allows explaining why it was possible to achieve success with the use of "heavy" rare earth elements – their size due to the mentioned effect is close to the ionic radius of the cation of the semiconductor lattice.

However, further studies conducted with crystals doped with "heavy" lanthanides revealed the instability of the resulting solid solutions – their decay. As expected, the most "long-lived" was doped with an ytterbium sample.

For example, the EPR spectrum that identified the tetragonal center of ytterbium registered at temperatures of $T < 4.5K$ immediately after the synthesis of the InP $<$Yb$>$ sample [4] could not be reproduced after six months.

An even shorter "lifetime" was given to a solid solution of gadolinium in indium phosphide, the EPR spectrum of which was recorded on the ER-220D unit in the temperature range from 3 to 300 K and showed a close to ideal angular dependence of a single gadolinium center in the $^8S_{7/2}$ state. Disintegration of the InP$<$Gd$>$ solid solution with a concentration of rare earth impurity of $4 \cdot 10^{16}$ cm$^{-3}$ occurred within a month.

Thus, solid solutions of lanthanides containing InP $<$Gd$>$ rare earth elements as substitutional impurities in the cationic lattice sites of III – V crystals completely lost their initial properties in a relatively short period of time.

All attempts to detect single impurity centers of lanthanides in A$^{III}$B$^{V}$ crystals doped with rare earth elements, with the exception of Yb, Er and Gd, by measuring the temperature dependence of static magnetic susceptibility and by the EPR method, failed [3].

Further studies showed the temperature dependence of the static magnetic susceptibility of A$^{III}$B$^{V}$ crystals containing lanthanides with the possible exception of europium in thermodynamical equilibrium. States of the materials under study receive an adequate description if we assume that rare earth impurities form in the crystal a system of weakly interacting quasimolecules such as Ln$_2$O$_3$ - quasimolecular centers, in which exchange interactions occur between atoms of rare earth elements [3]. The proposed model corresponds to the nature of temperature dependences of static magnetic susceptibility in a wide temperature range, demonstrating almost complete absence of dependence on the strength of the external magnetic field.
On a competitive basis, along with weakly interacting quasimolecules, "regions of spontaneous polarization – coupled spin-polarons" can be formed [1, 8-10]. The formation of spin-polarons occurs when ten or more quasimolecules fall into the orbit of a small donor. This becomes possible at low temperatures and in the region of high local concentrations [1, 8, 14] of rare earth elements (Figure 1).

![Figure 1](image)

**Figure 1.** Temperature dependence of magnetization of InP< Er > crystals with high erbium concentration, demonstrating magnetic anomalies caused by ferro-ordering of quasi-molecular centers

However, even in the composition of quasimolecular rare earth centers, due to the unique structure of the magnetic 4f-shell of the rare earth ion, shielded by 5s and 5p-electrons, is slightly distorted (split) by the electric field of ligands. This makes it possible to observe the processes of intracenter luminescence due to the presence of an effective excitation and absorption channel in almost any matrix, since the influence of the latter will be relatively weak [2, 8]. In this case, the spectra of intracenter luminescence will be formed by a set of narrow lines (~10 Å) due to the fact that the basic states of rare earth impurities will be practically not hybridized with the zone states of the crystal, and the excited ones will be weakly hybridized [2, 4, 6,11-13].

At the same time, a further increase in the concentration of the introduced rare earth impurity significantly changes the situation, demonstrating the chemical activity of rare earths and leading to the formation of "second phase inclusions" in the studied crystals, which were identified by the characteristic temperatures of the phase magnetic transitions.
4. Conclusion
Using the mentioned temperature dependences of magnetization of crystals of indium phosphides doped with neodymium (Figure 2), characteristic features are clearly observed. This may be due to strong magnetic "inclusions of the second phase" with residual impurities, which are part of the main lattice, in this case – with phosphorus [1].

The behavior of rare earth impurities in low-dimensional semiconductor structures is the subject of separate studies.

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