

ELECTRICAL PROPERTIES OF ZnSe CRYSTALS DOPED WITH TRANSITION METALS

A. N. Avdonin, G. V. Kolibaba, D. D. Nedeoglo*, N. D. Nedeoglo, V. P. Sirkeli

Department of Physics, State University of Moldova, A. Mateevich str. 60, MD-2009 Kishinev, Moldova

Hall effect in n-ZnSe single crystals doped with Cu, Ag or Au transition metals is studied in the temperature range from 55 to 500 K. A sign inversion of the Hall coefficient at $T > 300$ K is observed for the crystals doped with Cu, in contrast to the samples doped with Ag and Au. The measurements of electrical parameters show that silver manifests itself as an usual compensating acceptor impurity (Ag_{Zn}), while gold is an amphoteric impurity, which forms both donors (Au_i) and simple (Au_{Zn}) or associative acceptors. The model, which explains the existence of the Hall coefficient anomaly in n-ZnSe:Zn:Cu crystals and its lack in n-ZnSe:Zn:Ag and n-ZnSe:Zn:Au crystals, is proposed. It is shown that Cu exists in n-ZnSe in two charge states: Cu_{Zn}^+ (d^{10}) and $\text{Cu}_{\text{Zn}}^{++}$ (d^9), while Ag and Au exist in a singly charged state: Ag_{Zn}^+ (d^{10}) and Au_{Zn}^+ (d^{10}).

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1. Introduction

Transition metals introduced into ZnSe single crystals isoelectronically substitute Zn atoms and form deep acceptor levels in the band gap. Due to specific peculiarities of the electronic structure of d-elements such as Cu, Ag, and Au, the occupation ordering of d and s electron shells in free atoms of these elements is broken. As a result, these acceptor impurities can be in two charge states in zinc selenide: Cu_{Zn}^+ , Ag_{Zn}^+ , Au_{Zn}^+ with d^{10} electron configuration [1-4] and $\text{Cu}_{\text{Zn}}^{++}$, $\text{Ag}_{\text{Zn}}^{++}$, $\text{Au}_{\text{Zn}}^{++}$ with d^9 electron configuration [5-7]. Due to mixing of d, p and s states, the energy levels, formed by these impurities in the band gap, are electrically and optically active.

On the other hand, rapid cooling of the samples after their annealing is a favourable condition for the formation of interstitial defects. As the number of dopant element increases, the probability of the formation of interstitial donors such as Cu_i , Ag_i , and Au_i increases. This is caused by the fact that the difference between the ionic radii of these elements (0.96 Å (Cu), 1.13 Å (Ag), 1.37 Å (Au) [8]) and zinc (0.83 Å [8]) essentially increases with increasing the element number. Silver and gold atoms strain zinc sublattice when substituting zinc atoms, since their dimensions exceed the dimensions of zinc vacancy. The interatomic distance in zinc sublattice ($d(\text{Zn} - \text{Zn}) = 4.01$ Å) is essentially greater than the ionic radii of Ag and Au atoms, therefore, these atoms form mainly interstitial defects. The impurities, which can be both substitution and interstitial defects and form both acceptor and donor levels in the band gap, are chemically amphoteric impurities. Thus, amphoteric properties of Cu, Ag, and Au impurities in zinc selenide should become more apparent with increasing element number (i.e. from copper to gold).

The question about the charge state of Ag ions and the configuration of their electron shells in zinc selenide is open to discussion. It has been affirmed [1] that the copper impurity was more prone to the formation of the unoccupied d^9 -shell configuration than the silver and gold impurities because of smaller atomic number of Cu within the limits of the same isoelectronic line. The authors [1] suggested that Ag_{Zn}^+ and Au_{Zn}^+ ions had the usual d^{10} -configuration and the formation of $\text{Ag}_{\text{Zn}}^{++}$

* Corresponding author: nedeoglo@usm.md

and $\text{Au}_{\text{Zn}}^{++}$ ions with d^9 -configuration was impossible. At the same time, the authors [6,7] showed on the basis of ODMR investigations that $\text{Ag}_{\text{Zn}}^{++}$ and $\text{Au}_{\text{Zn}}^{++}$ ions had d^9 -configuration.

Recently [8] we have studied the luminescence properties of Au doped ZnSe crystals and discussed the nature of the luminescence centre.

Charge state of Cu, Ag and Au impurities in ZnSe, their electron shell configuration and amphoteric properties are discussed in the present paper on the ground of both the investigation of kinetic phenomena in ZnSe crystals doped with these impurities and the analysis of electric properties of the crystals depending on the dopant concentration.

2. Experimental data and discussion

Doping of n-ZnSe samples with Cu, Ag or Au was made during a long-term (100 h) high-temperature (950 °C) treatment of as-grown high-resistive ($\rho=10^8\div 10^9 \Omega\cdot\text{cm}$) single crystals in Zn+Cu, Zn+Ag or Zn+Au melts with various dopant contents. The doping level was varied by changing the dopant content in Zn melt from 0.05 to 0.75 at% Cu, 0.1 to 15 at% Ag or 0.05 to 10 at% Au. Annealing was made in evacuated quartz ampoules placed into a vertical furnace. After annealing, the ampoules were turned over and immersed in cold water for rapid cooling of the samples down to room temperature. The sample surface was etched in 7% bromine-methanol solution and then boiled in 40% NaOH solution. Ohmic indium contacts were used for electrical measurements. Hall effect was investigated in the temperature range from 77 to 300 K.

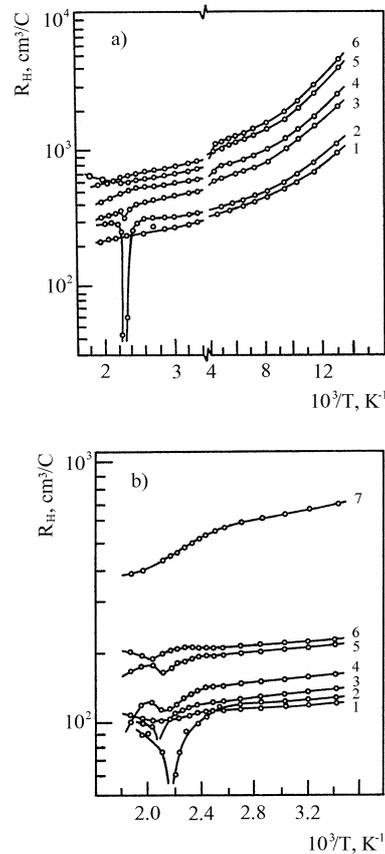


Fig. 1. Temperature dependence of the Hall coefficient for n-ZnSe:Zn:Cu crystals. Cu content in Zn melt, at%: a) 1–0, 2–0.05, 3–0.1, 4–0.3, 5–0.4, 6–0.5 (series A); b) 1–0, 2–0.05, 3–0.1, 4–0.2, 5–0.3, 6–0.5, 7–0.75 (series B).

The temperature dependence of the Hall coefficient for the Cu-doped samples is shown in Fig.1. “Series A” and “series B” differ by the concentration of native defects in the as-grown

crystals. In the temperature range from 77 K to 300 K (Fig. 1a), the character of the $R_H=f(10^3/T)$ dependence is unchanged with increasing Cu content in Zn melt: the Hall coefficient decreases with increasing temperature. This is caused by the activation of electrons from shallow donor states of a non-controlling impurity to the conduction band. The $R_H=f(10^3/T)$ dependence becomes weaker and tends to saturation near 300 K. However, further increase of temperature leads again to a decrease of R_H followed by new saturation. This is caused by ionisation of a deeper donor level and its exhaustion.

The character of the $R_H=f(10^3/T)$ dependence is essentially changed for $T>380$ K (Fig. 1b). For the sample annealed in pure Zn melt, the Hall coefficient decreases slightly and monotonously as the temperature increases. The addition of 0.05 at.% Cu into Zn melt considerably changes the character of the $R_H=f(10^3/T)$ dependence. While the temperature increases up to 370 K, this dependence follows the curve for as-grown sample with the difference that R_H has higher values. Further increase of the temperature leads to a sign inversion of the Hall coefficient (Fig. 1, curve 2).

Increasing Cu content in the investigated samples first slightly shifts the temperature of the R_H sign inversion towards high temperatures and then leads to a gradual disappearance of this peculiarity in the $R_H=f(10^3/T)$ dependence.

The temperature dependence of the Hall coefficient for the Ag-doped samples is shown in Fig. 2. The curves have the typical form for samples with several local donor levels. The Hall coefficient decreases exponentially with temperature rise due to electron activation from the shallowest donor level (Fig. 2, curves 1-6). Then the curves tend to saturation at temperatures above 100 K due to exhaustion of this donor level. The increase of temperature above 300 K leads again to an exponential decrease of the $R_H=f(10^3/T)$ dependence with far larger slope than in the low-temperature part of the curve. The activation of electrons from the second deeper donor level takes place in this temperature range. This donor level is also exhausted at temperatures above 500 K. The slopes of the exponential parts allow for the determination of the energetic depths of corresponding donor levels.

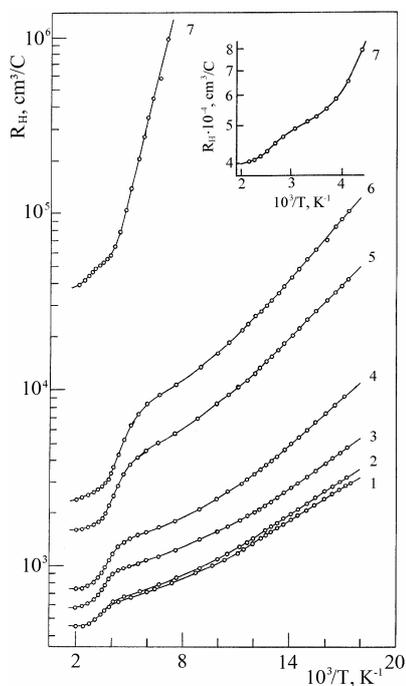


Fig. 2. Temperature dependence of the Hall coefficient for n-ZnSe:Zn:Ag crystals. Ag content in Zn melt, at%: 1 – 0, 2 – 1, 3 – 2, 4 – 5, 5 – 10, 6 – 12, 7 – 15. (Inset): the high-temperature range of the dependence for sample 7.

Increasing Ag content in the samples leads to a shift of the $R_H=f(10^3/T)$ dependence towards greater values of the Hall coefficient. Thereby, the compensating action of Ag impurity manifests itself. A shift of the onset of electron activation from the deeper donor level towards low

temperatures is also observed. This is stipulated by the fact that the compensation degree of the shallow donor level increases and the contribution of this level to the total concentration of charge carriers in the conduction band decreases. Therefore, the activation process from the second deeper donor level manifests itself more distinctly. As the compensation degree increases, the part of the exponential curve shifts towards the lower temperatures and its length increases too. The presence of the deeper donor level is most clearly revealed at the maximum Ag content in the melt (Zn+15 at.% Ag). The resistivity of this sample increases sharply because of the very high compensation degree of the shallow donors. The Hall coefficient measurements in the low temperature range are thus hampered, and we cannot observe the activation process from the shallow donor level (Fig. 2, curve 7). However, the exponential decrease of R_H is observed again after exhaustion of the second donor level (Fig. 2, inset), which indicates the presence of the third deepest donor level. A tendency to exhaustion of this level is observed at $T \approx 500$ K.

Fig. 3. shows free electron concentration in the gold-doped ZnSe single crystals versus temperature. For the lightly doped crystals (Fig. 3, curve 1), the $n=f(10^3/T)$ dependence is typical for the samples with two electrically active donor levels. As temperature decreases to 180 K, the electron concentration decreases due to “freezing” of electrons to unknown deep donor level. At smaller temperatures, the number of electrons on these deep donor levels is negligible in comparison with the number of ionised shallow donors. As a result, the $n=f(10^3/T)$ dependence flattens in the temperature range from 180 to 130 K. The further temperature decrease down to the 77 K leads to an exponential decrease of the electron concentration due to “freezing” of electrons to the shallow donor level.

As Au content in Zn+Au melt increases to 0.5 at%, free electron concentration also increases in all the investigated temperature range (Fig. 3, curves 2). The further increase of Au content in the melt results in a decrease of the electron concentration (Fig. 3, curves 3-5). Consequently, gold in ZnSe manifests itself as a chemically amphoteric impurity: a donor impurity at low Au concentration and a compensating acceptor impurity at higher Au concentration.

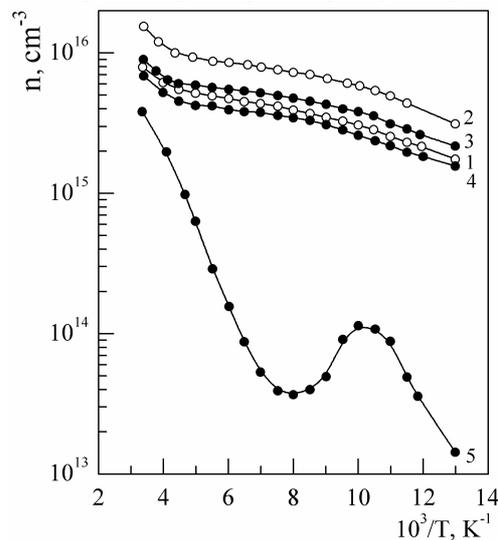


Fig. 3. Temperature dependence of electron concentration for n-ZnSe:Zn:Au crystals. Au content in Zn melt, at%: 1 – 0.05, 2 – 0.5, 3 – 2, 4 – 5, 5 – 10.

The most interesting $n=f(10^3/T)$ dependence is observed for the sample with maximum Au concentration (Fig. 3, curve 5). As temperature decreases from 300 to 150 K, the electron concentration rapidly decreases under the exponential law due to “freezing” of electrons to the deep donor level. We suppose that such a high gold concentration (10 at% Au) promotes the formation of a great number of Au_{Zn} acceptors, which compensate shallow donor level. Consequently, the concentration of electrons activated from the deep donor level rapidly decreases with decreasing temperature. As a result, the sample resistivity increases. At temperatures below 150 K, the part of the curve with anomalous behaviour is observed in the $n=f(10^3/T)$ dependence. After our opinion, this anomaly is caused by the effect of electron gas heating in strong electric field ($\sim(10\div30)$ V/cm),

which appears in the sample at $T > 150$ K due to rapid increase of its resistivity. In the strong electric field, free electrons acquire energy enough for ionisation of the impurity atom by collision. As a result, free electron concentration increases in the temperature range from 125 to 100 K (Fig. 3, curve 5) and the sample resistivity decreases. The intensity of ionisation by collision diminishes and the electron concentration again decreases due to “freezing” of electrons to ionised impurity centres.

3. Conclusions

We have proposed a model [9] that explains the anomalies of kinetic coefficients with the specificity of energy levels of transition metal impurities in n-ZnSe. The essence of this model is the presence of two energy levels of acceptor type that correspond to two charge states of the impurity, for instance Cu_{Zn}^+ (d^{10}) and $\text{Cu}_{\text{Zn}}^{++}$ (d^9). The shallowest $\text{Cu}_{\text{Zn}}^{++}$ level with energetic depth of 0.35 eV [2] is completely occupied by electrons, while the deeper Cu_{Zn}^+ level with energetic depth of 0.73 eV [2] is empty at low temperatures. The thermal activation of electrons from the valence band to this vacant level becomes effective at sufficiently high temperatures ($T > 400$ K, Fig. 1, curve 2). The free hole concentration in the valence band sharply increases, but the concentration of electrons in the conduction band is constant due to exhaustion of the donor impurity. Thus, we observe electron-hole impurity conductivity that is the condition necessary for a sign inversion of the Hall coefficient in p- and n-type semiconductors [10]. The anomalous $R_H = f(10^3/T)$ dependence flattens and completely disappears with increasing Cu content due to the redistribution of Cu_{Zn}^+ and $\text{Cu}_{\text{Zn}}^{++}$ centre concentrations towards a decrease of Cu_{Zn}^+ centres responsible for the hole concentration in the valence band and an increase of $\text{Cu}_{\text{Zn}}^{++}$ centres [9].

The anomaly in temperature dependence of the Hall coefficient in n-ZnSe:Zn:Cu samples in the high-temperature range is therefore explained by the existence of Cu atoms on Zn sublattice sites in two charge states with d^9 and d^{10} electron configuration. The number of electrically active interstitial Cu_i donors in n-ZnSe:Zn:Cu crystals is insufficient for revealing amphoteric properties of Cu impurity. That is why the free electron concentration decreases monotonously with increasing Cu content, which indicates purely acceptor properties of Cu impurity in n-ZnSe. Interstitial Cu atoms form only associative acceptors ($\text{Cu}_{\text{Zn}}-\text{Cu}_i$), ($\text{Cu}_{\text{Zn}}-\text{V}_{\text{Se}}-\text{Cu}_i$) [11].

Thus, electrical measurements show that Ag and Au ions form simple singly charged Ag_{Zn}^+ and Au_{Zn}^+ acceptors with d^{10} electron configuration, while Cu ions form both singly charged Cu_{Zn}^+ and $\text{Cu}_{\text{Zn}}^{++}$ with d^{10} and d^9 acceptors. Therefore, copper impurity forms two acceptor levels, while silver and gold impurities form single-energy levels near the valence band. The measurements of electrical parameters show that silver manifests itself as a usual compensating acceptor impurity (Ag_{Zn}), while gold is an amphoteric impurity, which forms both donors (Au_i) and simple (Au_{Zn}) or associative acceptors.

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