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Zinc Impurity Atoms in GaP, GaAs, and GaSb Examined with Mössbauer Spectroscopy

Mössbauer spectra of $^{67}Ga(^{67}Zn)$ and $^{67}Cu(^{67}Zn)$ impurity atoms in the bulk of GaP, GaAs, and GaSb samples correspond to isolated zinc centers at Ga sites. The observed shift of the spectral centers of gravity to higher positive velocities at the transition from p- to n-type samples corresponds to the recharging of a shallow zinc impurity center. Mössbauer spectra of $^{67}Cu(^{67}Zn)$ impurities at the surface of samples represent a superposition of spectra corresponding to isolated zinc centers at gallium sites with those corresponding to zinc associates with an arsenic vacancy.

Keywords: Mössbauer spectroscopy, impurity atoms, zinc.

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ПРИМЕСНЫЕ АТОМЫ ЦИНКА В GaP, GaAs И GaSb, ИЗУЧЕННЫЕ МЕТОДОМ МЁССБАУЭРОВСКОЙ СПЕКТРОСКОПИИ

Мессбауэровские спектры примесных атомов $^{67}Ga(^{67}Zn)$ и $^{67}Cu(^{67}Zn)$ в объемной части образцов GaP, GaAs и GaSb отвечают изолированным центрам цинка в узлах галлия. Наблюдается сдвиг центра тяжести спектров в область положительных скоростей при переходе от дырочных к электронным образцам, и это соответствует перезарядке мелкого примесного центра цинка. Мессбауэровские спектры примесных атомов $^{67}Cu(^{67}Zn)$ в приповерхностной области образцов представляют собой суперпозицию спектров, отвечающих изолированным центрам цинка в узлах галлия, и спектров, отвечающих ассоциатам цинка с вакансией мышьяка.

Ключевые слова: мессбауэровская спектроскопия, примесные атомы, цинк.

It is well known that a zinc impurity in III-V compounds forms shallow acceptor levels (0.02–0.04 eV above the valence band edge) [6]. A study of zinc impurity atoms in GaP, GaAs, and GaSb using emission Mössbauer spectroscopy of the $^{67}Ga(^{67}Zn)$ isotope opens the way to revealing the effect of electrical activity of "daughter" atoms (with the evident inactivity of "parent" atoms) on the Mössbauer spectral parameters of the ^{67}Zn probe, whereas the relevant spectra of the $^{67}Cu(^{67}Zn)$ isotope make possible the study of a similar effect for both daughter and parent atoms [1–5; 7]. According to [6], a copper impurity forms shallow donor levels in III-V compounds (in GaAs, they lie at ~ 0.07 eV below the conduction band edge) and deep two-electron acceptor levels (~ 0.14 and 0.44 eV above the valence band edge in GaAs).

The samples under study were single-crystal GaP ($n = 2 \times 10^{18}$ sm^{-3}, $p = 3 \times 10^{18}$ sm^{-3}), GaAs ($n = 10^{17}$ sm^{-3}, $p = 5 \times 10^{16}$ sm^{-3}), and GaSb ($n = 8 \times 10^{18}$ sm^{-3}, $p = 5 \times 10^{18}$ sm^{-3}). The samples were doped with the radioactive isotopes ^{67}Ga and ^{67}Cu through diffusion annealing in vacuum for 5 h, at temperatures 100°C lower than the melting temperature of the respective compound. To prevent the evaporation of volatile components, a powder of the corresponding compound was introduced into an ampule. The maximum Zn concentration that formed after the radioactive decay of parent ^{67}Ga and ^{67}Cu atoms did not exceed 10^{15} sm^{-3} (i.e., the Fermi level position in all the samples was determined by the background dopant). The spectra were recorded either without the preliminary treatment of the sample surface (these spectra were associated with the impurity atoms located in the surface region) or an ~50-μm-thick layer was removed from the sample surface prior to the recording of spectra, and these spectra were assigned to impurity atoms in the sample bulk.

^{67}Zn Mössbauer spectra were recorded using a commercial spectrometer with a modified driving system [4; 5]. A PZT-ceramics piezoelectric converter served as a modulator. The spectra were recorded at 4.2 K using a ^{67}ZnS absorber, which served as a reference for all the experimental spectra. The spectra typical of the bulk and surface regions are shown in Figs. 1, 2, 3 and 4, and the results of data processing for the bulk samples are presented in the table.

^{67}Ga(^{67}Zn) spectra recorded from the bulk of samples are single lines with a full width at half-maximum (FWHM) close to the instrumental broadening 2.6(3) μm/s, and their position (center of gravity) shifts steadily to higher velocities at the transition from GaP to GaSb. The line position slightly depends on the type of sample conduction: it shifts to a lower velocity at the transition from electron to hole conduction, and this effect is most evident in wide-gap materials.

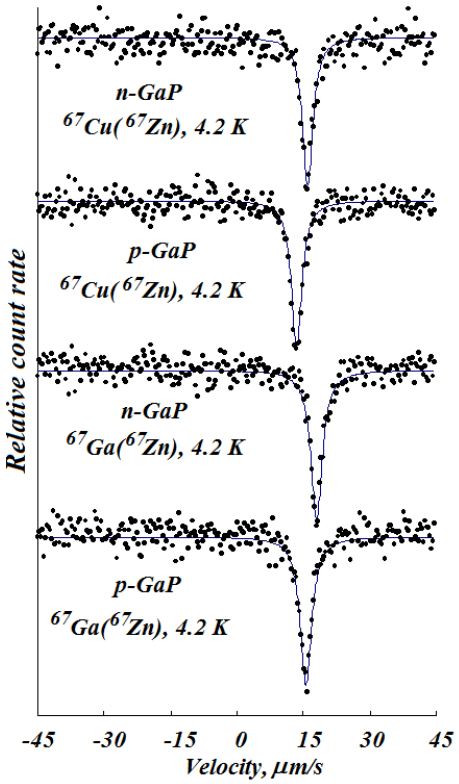

Fig. 1. Emission Mössbauer spectra of ^{67}Ga(^{67}Zn) impurity atoms for n-type and p-type samples GaP

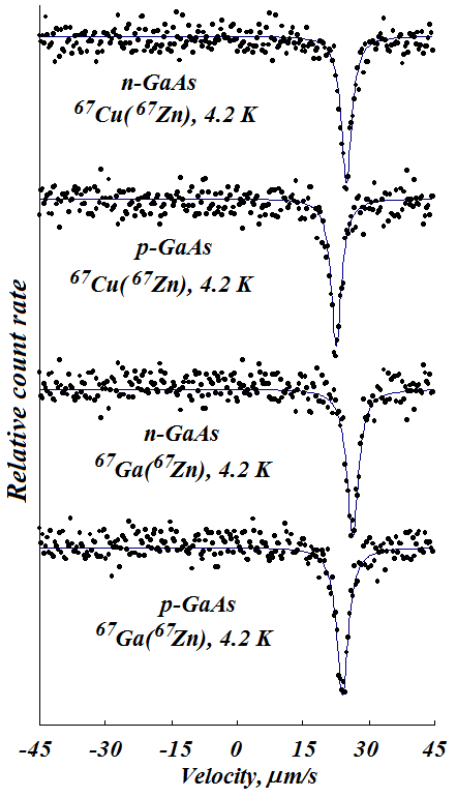

Fig. 2. Emission Mössbauer spectra of ^{67}Ga(^{67}Zn) impurity atoms for n-type and p-type samples GaAs

The center of gravity position in the Mössbauer spectrum depends on two factors: the electron density at the nucleus of ^{67}Zn under study, and the second-order Doppler shift defined by the Debye temperature of a crystal [1–3; 7]. Since the Debye temperature is independent of the conduction type, we conclude that the recharging of a shallow impurity level influences the electron density near a ^{67}Zn nucleus: the electron density increases at the transition from p- to n-type samples, which corresponds to the transition $[Zn^0] \rightarrow [Zn^{2-}]$. ^{67}Ga(^{67}Zn) Mössbauer spectra should be related to isolated Zn impurity centers at Ga sites, whereas the positive shift of the spectral centroid along the series GaP-GaAs-GaSb reflects the variation of the chemical bond ionicity of zinc atoms with respect to the atoms in the first coordination sphere of a zinc atom.

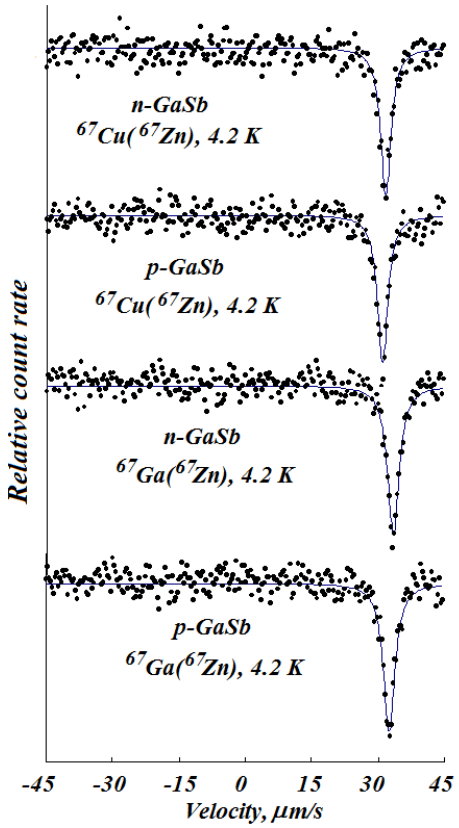

Fig. 3. Emission Mössbauer spectra of ^{67}Ga(^{67}Zn) impurity atoms for n-type and p-type samples GaSb

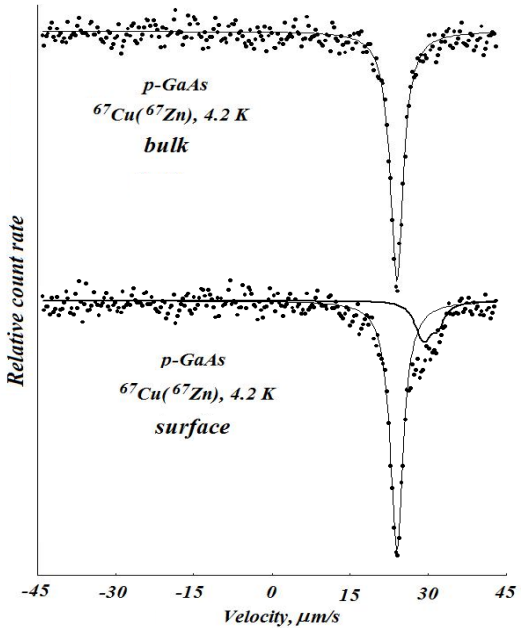

Fig. 4. Emission Mössbauer spectra of ^{67}Cu(^{67}Zn) impurity atoms in bulk and surface region of p-type GaAs

Parameters of ^{67}Ga(^{67}Zn) and ^{67}Cu(^{67}Zn) Mössbauer spectra in GaP, GaAs, and GaSb at 4.2

Compound	^{67}Ga(^{67}Zn) spectra		^{67}Cu(^{67}Zn) spectra	
	centroid of the spectrum, μm/s	FWHM, μm/s	centroid of the spectrum, μm/s	FWHM, μm/s
n-GaP	16.0(4)	2.8(3)	18.0(4)	3.1(3)
p-GaP	13.5(4)	2.7(3)	15.6(4)	2.8(3)
n-GaAs	24.9(4)	2.7(3)	26.3(4)	3.0(3)
p-GaAs	22.6(4)	2.6(3)	24.0(4)	3.0(3)
n-GaSb	31.5(4)	2.8(3)	33.2(4)	3.0(3)
p-GaSb	30.8(4)	2.6(3)	32.5(4)	2.7(3)

The spectra of ^{67}Cu(^{67}Zn) impurity atoms in the bulk of the samples are also single lines corresponding to isolated Zn centers at Ga sites. Similarly to ^{67}Ga(^{67}Zn) spectra, the center of gravity shifts to positive velocities at the transition from p- to n-type samples (this shift is associated with the transition $[Zn^0] \rightarrow [Zn^{2-}]$).

As in the case of ^{67}Ga(^{67}Zn) spectra the center of gravity of ^{67}Cu(^{67}Zn) spectra is in the region of positive velocities for GaP-GaAs-GaSb compounds. It is possible that this shift is due not only to changes in ionicity of bond of zinc impurity atoms with atoms in its local environment, but metallization of these bonds. In particular, in Fig. 5 shows the dependence of the central shift on the band gap of used semiconductors and extrapolation of this dependence on the zero band gap gives the value of the central shift 38.5(9) mm/s, which is typical of ^{67}Zn intermetallic compounds of zinc.

The electrical activity of copper impurity atoms does not affect the fine structure of spectra for the bulk of the samples. In the surface region, the spectra of ^{67}Cu(^{67}Zn) impurity atoms demonstrate a superposition of the above-described single lines related to isolated Zn atoms at Ga sites and a quadrupole triplet (GaAs: spectrum center of gravity 30(1) μm/s, quadrupole coupling constant 0.92(3) MHz, line width 3.0(3) μm/s). The last spectrum is presumably related to the associates of zinc impurity centers with As vacancies (these associates were identified in the study of photoluminescence in GaAs:Cu [6]).

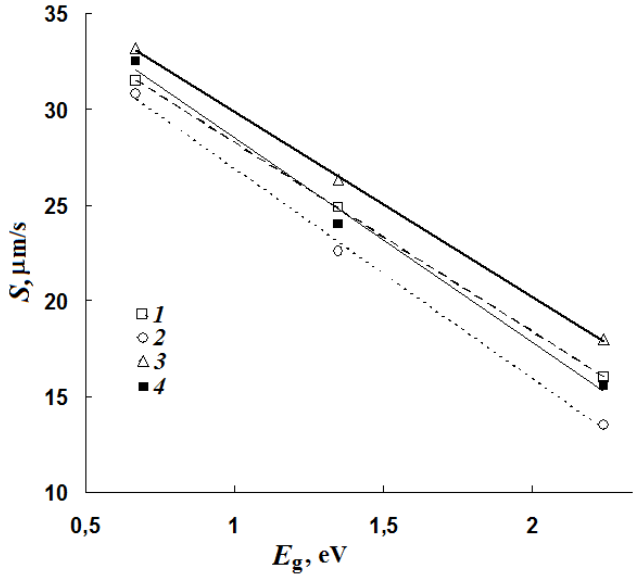

Fig. 5. The dependence of the gravity center S of ^{67}Cu(^{67}Zn) (*1*, *2*) and ^{67}Ga(^{67}Zn) (*3*, *4*) on the band gap E_g of n-type (*1*, *3*) and p-type (*2*, *4)* semiconductors

Thus, the Mössbauer spectra of ^{67}Ga(^{67}Zn) and ^{67}Cu(^{67}Zn) impurity atoms in the bulk of GaP, GaAs, and GaSb samples are related to isolated zinc centers at Ga sites, and the recharging of Zn impurity centers is observed. Mössbauer spectra of ^{67}Cu(^{67}Zn) impurities at the surface of samples are related to isolated zinc centers as well as zinc associates with arsenic vacancies.

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Quasiparticles, Spectral Functions, and Kinetic Equation in Quantum Fermi Liquid Theory

Green's function method in Kadanoff-Baym version is used to analyze different ways of determining of quasiparticle energies in a normal quantum system of interacting fermions and to derive equations which determine these energies. The appearing differences for the microscopic and phenomenological approaches to the Fermi liquid theory are discussed. The validity of the Landau-Silin kinetic equation for the quasiparticle distribution function at finite temperature is proved on the basis of a proper approximation to the spectral function.

Keywords: Fermi liquid, Green's function, spectral function, quasiparticle, kinetic equation.