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A STUDY OF IRON IMPURITY ATO MS IN GAAS AND GAP APPLYING THE METHOD OF EMISSION MÖSSBAUER SPECTROSCOPY

Mössbauer emission spectroscopy of the $^{57}Co(^{57m}Fe)$ isotope is used to find the dependence of the charge state of Fe impurity atoms in GaAs and GaP on the Fermi level position in the band gap. The iron atoms substitute gallium atoms and have a tetrahedral surrounding. The electron configuration for a neutral state of these centres Fe^0 is $3d^54s^{0.52}p^{1.56}$ (in GaAs) or $3d^54s^{0.79}p^{2.37}$ (in GaP), while in the ionized state the population of the 3d shell of iron is increased ($3d^6$). A value $E_{Fe} − E_{Co} = −(0,016 \pm 0,003)$ eV has been obtained for GaAs and $E_{Fe} − E_{Co} = −(0,035 \pm 0,003)$ eV for GaP. The process of fast electron exchange via the valence band between the Fe^0 and $Fe^−$ centres at 295 K is observed in slightly overcompensated GaAs and GaP .

Keywords: impurity atoms, electron exchange, Mössbauer emission spectroscopy.

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ИССЛЕДОВАНИЕ ПРИМЕСНЫХ АТОМОВ ЖЕЛЕЗА В GaAs И GaP МЕТОДОМ ЭМИССИОННОЙ МЁССБАУЭРОВСКОЙ СПЕКТРОСКОПИИ

Эмиссионная мессбауэровская спектроскопия использована для обнаружения зависимости зарядового состояния примесных атомов Fe в GaAs и GaP от положения уровня Ферми в запрещенной зоне. Атомы железа замещают атомы галлия и имеют тетреаэдрическое окружение. Электронная конфигурация нейтрального состояния центров Fe^0 $3d^54s^{0.52}p^{1.56}$ (в GaAs) или $3d^54s^{0.79}p^{2.37}$ (в GaP), тогда как в ионизованном состоянии засе-

ленность 3d оболочки железа возрастает (3d^6). Значение $E_{Fe} - E_{Co} = -(0.016 \pm 0.003)$ эВ получено для GaAs и $E_{Fe} - E_{Co} = -(0.035 \pm 0.003)$ эВ для GaP. Процесс быстрого электронного обмена через валентную зону между центрами Fe^0 и Fe$^-$ при 295 K наблюдался для слабо перекомпенсированных GaAs и GaP.

Ключевые слова: примесные атомы, электронный обмен, эмиссионная мессбауэровская спектроскопия.

1. Introduction

The Mössbauer effect provides a perspective method for the study of the state of impurity atoms in solids [1]. The parameters of the Mössbauer spectra make it possible to define the charge state of impurity atoms, their electronic structure, their position in the lattice, the symmetry of the local surroundings, and the formation of various associates of the impurity atoms with lattice defects.

In this study, the potentials of the emission Mössbauer spectroscopy of the ^{57}Co(^{57m}Fe) isotope are used to identify neutral and ionized states of Fe impurity atoms in the bulk regions of GaAs and GaP, as well as to observe fast electron exchange between neutral and ionized Fe centers in the bulk region.

2. Experimental Procedure

The Mössbauer spectra were recorded at 80 and 295 K. As a conventional absorbent, we used K$_4$Fe(CN)$_6$.3H$_2$O with a surface density of 0.05 mg/sm^2 with respect to the ^{57}Fe isotope. The apparatus width of the spectral line was $G = (0.26 \pm 0.02)$ mm/s. The isomer shifts δ are given relative to K$_4$Fe(CN)$_6$.3H$_2$O. The error of the isomer shift measurement was $\pm$ 0.01 mm/s, that of the linewidth G measurement $\pm$ 0.02 mm/s.

The starting materials were GaAs ($p = 2.2 \times 10^{18}$ sm^{-3}, $n = 9.0 \times 10^{17}$ sm^{-3}, $n = 5.0 \times 10^{16}$ sm^{-3} at 295 K) and GaP ($p = 1.0 \times 10^{18}$ cm^{-3}, $n = 9.0 \times 10^{17}$ sm^{-3} and $n = 5.0 \times 10^{16}$ sm^{-3} at 295 K) single crystals. Zinc was the acceptor impurity and tellurium was the donor one.

Cobalt was electrolytically deposited on the sample surface from an ammonium solution of the noncarrying preparation ^{57}CoCl$_2$. The diffusion process was held in evacuated quartz ampoules at 1050°C (GaAs) and 1150°C (GaP). After the diffusion process the samples were treated with a mixture of HNO$_3$ and HCl (to remove the remaining ^{57}Co that had not diffused in) and then $\approx$ 40 μm thick surface layer was removed. The samples prepared in this way were used as the Mössbauer sources.

3. Experimental Results and Discussion

3.1. The electron configuration of the Fe centre

In the emission variant of Mössbauer spectroscopy isotope ^{57}Co is introduced into the sample, the radioactive transformation of ^{57}Co (electron capture) results in the Mössbauer level ^{57m}Fe. Cobalt and iron create deep acceptor levels in GaAs and GaP [2].

When analyzing experimental results, one should bear in mind that $N_{Co} >> N_{Fe}$ (N_{Co} and N_{Fe} are the concentrations of Co and Fe impurity, respectively); hence, the position of the Fermi level in the band gap is governed by the concentrations of Co impurity atoms and dopant atoms, as well as by the type of their electric activity (Zn and Te are used as dopants to fabricate p- and n-type GaAs and GaP, respectively).

Let the starting sample be Te-doped. Then, if $N_{Te} > N_{Co}$ (where N_{Te} is the tellurium concentration) the Fermi level is at the bottom of the conduction band (at 295 to 80 K) and the iron centres are ionized Fe$^-$. If the starting sample is zinc-doped, the Fermi level will be at the top of the valence band (at 295 to 80 K) and the iron centres will be not ionized in this case Fe^0. In principle, the Mössbauer spectra for the two states Fe$^-$ and Fe^0 must have different isomer shifts.
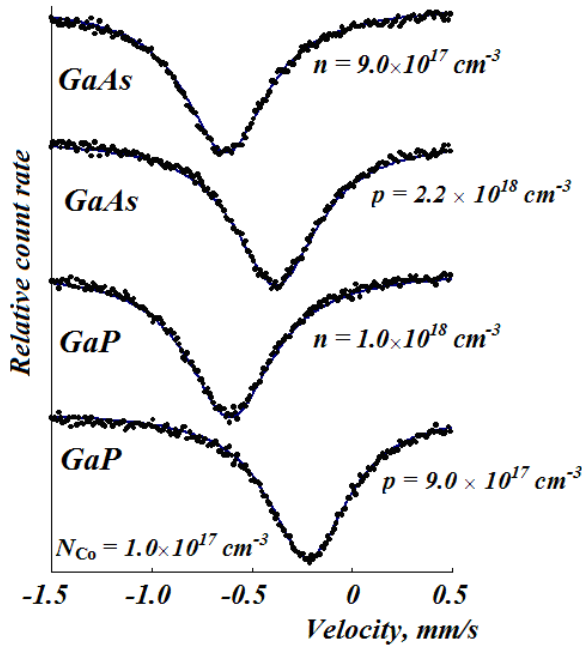
Fig. 1. Emission Mossbauer spectra of ^{57}Co(^{57m}Fe) in GaAs and GaP at 295 K

In order to prove this, Mössbauer spectra of ^{57m}Fe in GaAs were recorded for two different samples with N_{Co} =1.0 × 10^{17} sm^{-3}, N_{Te} = 9.0 × 10^{17} sm^{-3} and N_{Co} = 1.0 × 10^{17} sm^{-3}, N_{Zn} = 2.2 × 10^{18} sm^{-3} . For this purpose the diffusion was carried out for 24 h. The Mössbauer spectra at 295 K are shown in fig. 1, and the results of their treatment are given in table 1. As it is seen, both, the *n*-type and the *p*-type spectra consist of single rather broadened lines (*G* = 0.50 mm/s). The isomer shift values for *n*- and *p*-type samples are different. It is evident that the isomer shift of the ^{57m}Fe Mössbauer spectra in *p*-type GaAs corresponds to the non-ionized centres of iron Fe^0, while for the *n*-type samples it corresponds to the ionized Fe$^-$ centres. The absence of the quadrupole splitting in the Mössbauer spectra suggests cubic symmetry of the local surroundings of the iron atoms.

Table 1

The isomer shifts of the emission Mossbauer spectra of ^{57}Co(^{57m}Fe) in GaAs and GaP

Matrix	n, p (sm^{-3})	N_{Co} (sm^{-3})	δ (295 K) (mm/s)	δ (80 K) (mm/s)
GaAs	$n = 9.0 \times 10^{17}$	10^{17}	0.632	0.639
GaAs	$p = 2.2 \times 10^{17}$	10^{17}	0.381	0.385
GaP	$n = 9.0 \times 10^{17}$	10^{17}	0.610	0.615
GaP	$p = 1.0 \times 10^{18}$	10^{17}	0.220	0.240

The authors of [3] who have studied the state of iron atoms in GaAs by EPR measurements, concluded that iron substitutes for gallium and its electron configuration in the *p*-type samples is $3d^5$. The isomer shift of the Mössbauer spectra of ^{57m}Fe in *p*-GaAs samples differs from that assigned to a pure electron $3d^5$ configuration (according to [4] δ = 1.08 mm/s for $3d^5$). In other words, the electron configuration of the (Fe)^0 centre is not $3d^5$. Probably, substituting for gallium atoms in GaAs, the iron atoms make sp^3-hybrid bonds. The presence of the valence $4sp$ electrons in addition to the $3d^5$ shell on iron atoms results in the increase of the electron density at the ^{57}Fe nuclei, so that the electron configuration of the Fe^0 centre is $3d^54s^xp^{3x}$. If one neglects the effect of $4p$ electrons on the total electron density at ^{57}Fe nuclei and compares the experimental value δ for the Fe^0 centre in GaAs with that for iron ions having an electron configuration $3d^5$, one may find the number of $4s$ electrons. Indeed, the isomer shift of the Mössbauer spectrum of Fe^0 relative to that of iron with $3d^5$ electron configuration may be given as follows:

$$\delta=\alpha\left(\left|\Psi(0)\right|_1^2 - \left|\Psi(0)\right|_2^2\right)= \alpha\Delta\left|\Psi(0)\right|^2 ,$$

(1)

where α is a term which depends on the nucleus parameters, $|\Psi(0)|_1^2$ and $\|\Psi(0)\|_2^2$ are the total electron densities at the ^{57}Fe nuclei for the electron configurations $3d^5$ and Fe^0.

To find $\Delta|\Psi(0)|^2$ one must know the calibration constant α. The most reliable value of α is [4]: $\alpha = -0.23a_o^{-3}$ mm/s. Using it we may find the electron configuration of the Fe^0 centre to be $3d^5 4s^{0.52} p^{1.56}$.

In order to prove this, Mössbauer spectra of ^{57m}Fe in GaP were recorded for two different samples with $N_{Co} = 1.0 \times 10^{17}$ sm^{-3}, $N_{Te} = 1.0 \times 10^{18}$ sm^{-3} and $N_{Co} = 1.0 \times 10^{17}$ sm^{-3}, $N_{Zn} = 9.0 \times 10^{18}$ sm^{-3} (for this purpose the diffusion was carried out for 24 h). The Mössbauer spectra at 295 K are shown in figs. 2 and 3, and the results of their treatment are given in table 1. For the p-type samples and for the n-type samples the Mössbauer spectra are single lines, the transition from (Fe)^0 to (Fe)$^-$ is followed by the increase of the isomer shift (see table 1). The electron configuration of the p-type samples (Fe^0 centre) is $3d^5 4s^{0.79} p^{2.37}$ (the calculation procedure is the same as for GaAs).
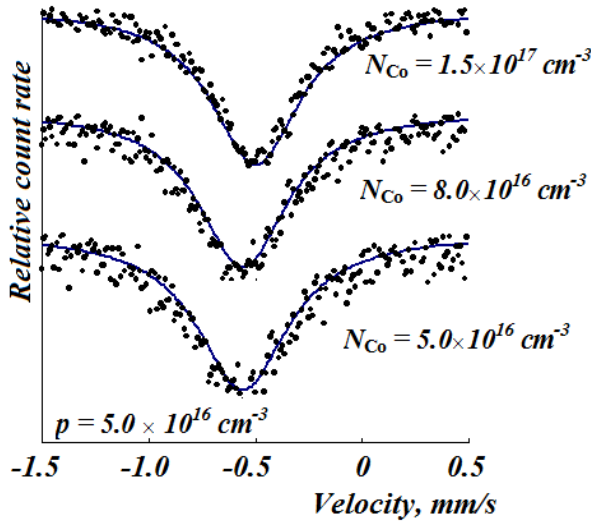

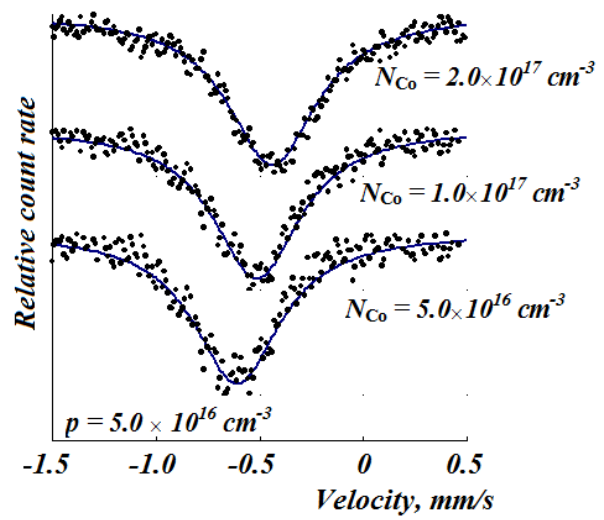Fig. 2. Emission Mossbauer spectra of ^{57}Co(^{57m}Fe) in GaAs at 295 K

Fig. 3. Emission Mossbauer spectra of ^{57}Co(^{57m}Fe) in GaP at 295 K

The decrease of the electron density at ^{57m}Fe nuclei after the transition from Fe^0 to Fe$^-$ in GaAs and GaP are explained by the increase of the iron $3d$ shell population ($3d^5 \rightarrow 3d^6$) following the ionization. However, if one assumes that the population of the iron valence $4sp$ shells of the Fe$^-$ is just the same as that of the Fe^0 centre, then the expected isomer shift of the Mössbauer spectra of Fe$^-$ in GaAs must be 1.05 mm/s and 0.95 mm/s for GaP, while the experimental values are ≈ 0.63 to 0.61 mm/s for the isomer shift of the Fe$^-$ centre. To reconcile the calculated and the experimental values of the Mössbauer isomer shifts of Fe$^-$ in GaAs and GaP we must assume that the sixth $3d$ electron on the Fe$^-$ centre occupies the atomic orbital $3d$ with a radius a little bit larger than that observed for a free ion. This results in less value of the isomer shift for the Fe$^-$ centre.

Thus, according to the Mössbauer data, the transition from Fe^0 to Fe$^-$ results in a change in the iron $3d$ shell population. This is in full agreement with the EPR data of [3], where an EPR spectrum was observed only for the non-ionized centres of iron Fe^0 (the electron configuration is $3d^5$), while for the ionized centres Fe$^-$ (the electron configuration is $3d^6$) no spectrum was observed even at 1.3 K due to the partial removal of the spin degeneracy of the ^5D state in a tetrahedral field.

3.2. The electron exchange between Fe^- and Fe^0

We have considered two extreme cases of the Fermi level position − one at the bottom of the conduction band and the other at the top of the valence band. Fe^- and Fe^0 correspond to these Fermi level positions. But of most interest is the case when the Fermi level is near the iron level and a partial iron centre ionization must be observed. There are two possible cases.

1. An average state will be observed in the Mössbauer spectrum, corresponding to fast electron exchange between Fe^0 and Fe^-.

2. The Mössbauer spectrum will correspond to the two iron states Fe^0 and Fe^-.

Let us discuss in details the conditions for\of a Mössbauer study of the charge exchange of the iron impurity centres. Evidently, for the Fermi level passing over the iron level at the quite low temperature (≈ 295 K) it is necessary to obtain a slightly overcompensated semiconductor ($N_{Co} \geq N_{Te}$), so that the Fermi level appears to be bound to the cobalt level E_{Co}:

$$\mu = E_{Co} - kT \ln\left[\beta_{Co} \frac{N_{Co} - N_{Te} - p + n}{N_{Te} + p - n} \right] \approx E_{Co} - kT \ln\left[\beta_{Co} \frac{N_{Co} - N_{Te}}{N_{Te}} \right], \tag{2}$$

where β_{Co} is the degeneracy factor of the cobalt level.

Equation (2) is valid if the concentration of free carriers can be neglected both compared with the difference $N_{Co} - N_{Te}$ and with $2 N_{Te}$. If the Fermi level is defined in this way, the equilibrium concentrations of the ionized Fe^- and non-ionized Fe^0 iron centres are defined as follows:

$$N_{Fe^-} = \frac{N_{Fe}}{1 + \frac{\beta_{Co}}{\beta_{Fe}} \frac{N_{Co} - N_{Te} - p + n}{N_{Te} + p - n} \exp\left(\frac{E_{Fe} - E_{Co}}{kT} \right)}, \tag{3}$$

$$N_{Fe^0} = N_{Fe} \frac{\frac{\beta_{Co}}{\beta_{Fe}} \frac{N_{Co} - N_{Te} - p + n}{N_{Te} + p - n} \exp\left(\frac{E_{Fe} - E_{Co}}{kT} \right)}{1 + \frac{\beta_{Co}}{\beta_{Fe}} \frac{N_{Co} - N_{Te} - p + n}{N_{Te} + p - n} \exp\left(\frac{E_{Fe} - E_{Co}}{kT} \right)}, \tag{4}$$

where E_{Fe} is the iron level energy and β_{Fe} its degeneracy factor.

Equations (3) and (4) are valid if the iron concentration is low enough not to affect the Fermi level position ($N_{Fe} << N_{Co}, N_{Te}, N_{Co} - N_{Te}$) which is the case when the Mössbauer spectra are observed.

From (3) and (4) one can easily obtain

$$P = \frac{N_{Fe^0}}{N_{Fe^-}} = \frac{\beta_{Co}}{\beta_{Fe}} \frac{N_{Co} - N_{Te} - p + n}{N_{Te} + p - n} \exp\left(\frac{E_{Fe} - E_{Co}}{kT} \right) \tag{5}$$

where $S = \frac{N_{Co} - N_{Te} - p + n}{N_{Te} + p - n} \approx \frac{N_{Co} - N_{Te}}{N_{Te}}$.

It is readily seen from this equation that in order to observe partial ionization of the iron centres in the Mossbauer spectra one must change the N_{Co} and N_{Te} ratio to fit $S \approx 1$. The pattern of the Mossbauer spectrum with $S \approx 1$ will depend on the relation between the time of Fe^- Fe^0 electron exchange and the lifetime of the Mossbauer level of ^{57m}Fe ($\tau_0 \approx 10^{-7}$ s). Two extreme cases are conceivable:

1. The time of the electron exchange is much smaller than τ_0. In this case the Mössbauer spectrum will be a single line with an isomer shift given by

$$\delta = \frac{\delta_{Fe^-} + P\delta_{Fe^0}}{P+1}$$ (6)

with δ_{Fe^0} and δ_{Fe^-} being the isomer shifts of the Mössbauer spectra corresponding to Fe^0 and Fe^-.

2. The time of the electron exchange is much larger than τ_0. As far as we use the emission variant of the spectroscopy, the electron capture results at first in the creation of multiply charged iron ions which turn to the Fe^0 state in a time much less than τ_0 and then slowly, during a time interval characteristic of the electron exchange, an equilibrium between Fe^0 and Fe^- is established. At the moment τ_0 the equilibrium is not yet established and the Mössbauer spectrum must correspond to the state Fe^0 only.

In order to observe the charge exchange process (i.e. to obtain a sample with $S \approx 1$) the diffusion was carried out into GaAs and GaP with $n = 5 \times 10^{16}$ sm^{-3} during 5 min. After the diffusion successive layers were removed from the sample by grinding, the cobalt concentration in the layers was 1.5×10^{17}, $8 \times \times 10^{16}$, 5×10^{16} sm^{-3} for GaAs and 2.0×10^{17}, 1.0×10^{17}, and 5.0×10^{16} sm^{-3} for GaP. The Mössbauer spectra at 295 K of all the layers were single rather broadened lines to correspond to centers Fe^0 (see fig. 3), their isomer shifts regularly decreased as the ratio $(N_{Co} - N_{Te})/N_{Te}$ increased (see table 2), i.e. the picture is a characteristic of fast electron exchange between the centres Fe^0 and Fe^-. Figure 4 shows the calculated dependence $P(S)$, which corresponds to the value of $\frac{\beta_{Co}}{\beta_{Fe}}\exp\left(\frac{E_{Fe}-E_{Co}}{kT}\right) = 0.53 \pm 0.03$ for GaAs and 0.25 ± 0.03 for GaP. Assuming that $\frac{\beta_{Co}}{\beta_{Fe}} \approx 1$ (since this value cannot differ much from unity), we obtain $E_{Fe} - E_{Co} = -(0.016 \pm 0.003)$ eV for GaAs and $E_{Fe} - E_{Co} = -(0.035 \pm 0.003)$ eV for GaP.

Table 2

The isomer shifts of the emission Mossbauer spectra of $^{57}Co(^{57m}Fe)$ in GaAs and GaP with various cobalt concentrations

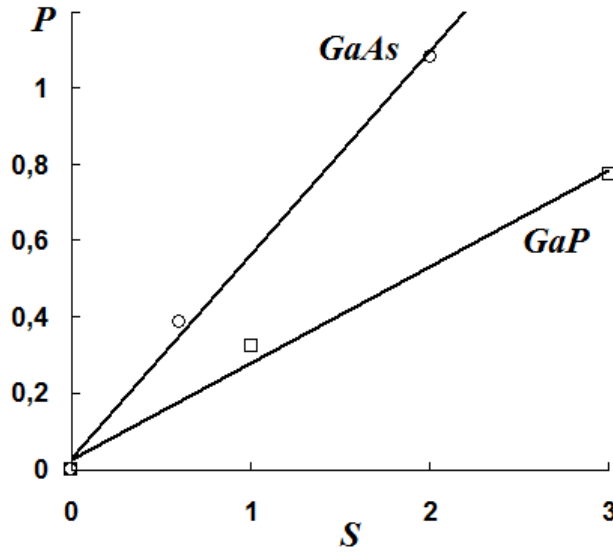| *Matrix*	N_{Te} (sm^{-3})	N_{Co} (sm^{-3})	δ (295 K) (mm/s)	δ (80 K) (mm/s)
GaAs	5.0×10^{16}	1.5×10^{17}	0.500	0.62
GaAs	5.0×10^{16}	8.0×10^{16}	0.562	0.63
GaAs	5.0×10^{16}	5.0×10^{16}	0.630	0.64
GaP	5.0×10^{16}	2.0×10^{17}	0.440	0.610
GaP	5.0×10^{16}	1.0×10^{17}	0.515	0.615
GaP	5.0×10^{16}	5.0×10^{16}	0.610	0.615

Fig. 4. Dependence of P on S for GaAs and GaP

The time of the electron exchange between Fe^- and Fe^0 in GaP and GaAs is, according to Mössbauer data, much less than 10^{-7} s. In the view of an acceptor character of the iron centres, the electron exchange process may be treated as a hole capture at the charged centre Fe^- and a subsequent removal of the hole to the valence band. Then the time of the exchange may be evaluated from the hole capture rate

$$\frac{1}{\tau_{Fe^-}} = p\sigma V, \tag{7}$$

where p is the hole concentration, V the thermal velocity, and σ their capture cross-section at the Fe^- centre.

At 295 K $p = 10^{15}$ sm^{-3} (according to Hall measurements), $V = 10^7$ sm/s, and using the value $\sigma \approx 10^{-13}$ sm^2 (the lower limit for Coulomb capture centres) we obtain $\tau_{Fe^-} \approx \tau_{Fe^0} \approx 10^{-9}\,s$, i.e. in a time interval $\tau_o \sim 10^2$ charge exchanges of the iron centre take place and an "average" iron state is observed in the Mössbauer spectrum.

At 80 K the Fermi level shifts (see equation (2)) and all the iron atoms are in an ionized state and a single line is observed in the Mössbauer spectrum, corresponding to Fe^- only (see table 2).

4. Summary

The iron impurity atom state in GaAs and GaP was studied by emission Mössbauer spectroscopy. The isomer shifts of the iron Mössbauer spectra in the p-type samples correspond to neutral centres Fe^0 with electron configuration $3d^5 4s^{0.52} p^{1.56}$ in GaAs and $3d^5 4s^{0.79} p^{2.37}$ in GaP. For n-type samples the isomer shifts move towards positive velocities and correspond to ionized centres Fe^- with six electrons on the $3d$ shell of iron.

For slightly overcompensated GaP samples at 295 K the process of fast electron exchange via the valence band between the centres Fe^0 and Fe^- was observed, the corresponding spectrum is a single line with an isomer shift depending on the Fermi level position. A value $E_{Fe} - E_{Co} = -(0.016 \pm 0.003)$ eV has been obtained for GaAs and $E_{Fe} - E_{Co} = -(0.035 \pm 0.003)$ eV for GaP.

In principle, the possibility to define the position of the impurity levels in the energy gap of semi-conductors is noted.

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