Identification of the double acceptor state of isolated nickel in gallium arsenide

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The zero-phonon line (ZPL) at 4615 cm^{-1} in the absorption spectrum of n-type GaAs:Ni has been measured under uniaxial stress and magnetic field. The observed ZPL splittings conclusively demonstrate that the ZPL is due to the $\Gamma_7(^2T_2)\rightarrow\Gamma_8(^2E)$ intracenter transition of isolated $Ni^+(3d^9)$, thus confirming that the doubly ionized state of the Ni acceptor is a stable charge state in n-type GaAs. The g factors of the ground state ($g_7=-1.16$) and of the excited state ($g_1=1.31$, $g_2=-0.29$) are analyzed in terms of the Jahn-Teller ϵ-mode coupling within the $^2T_2$ ground state.

I. INTRODUCTION

The study of point defects, especially transition-metal impurities in III-V compound semiconductors has been the subject of many experimental investigations during the last years.[1,2] Most transition metals in GaAs, GaP, and InP act as deep acceptors. In GaP, chromium,[3] iron,[4] and nickel[5] impurities have been shown to act also as double acceptors. In GaAs nickel has been suggested to be a possible double acceptor,[6] but a definite confirmation is still lacking. Nickel is also a subject of interest because it is used in the technology of contacts and being a fast diffusing impurity it is a classical contaminant of GaAs devices and its role has to be specified.

In the case of GaP:Ni the 0.664-eV absorption and luminescence zero-phonon line (ZPL) observed in n-type samples has been first attributed to a $Ni^{2+}(3d^8)$ intracenter transition.[7] However, Zeeman measurements and EPR results[5] show that the observed spectra correspond undoubtedly to the substitutional $Ni^+(3d^9)$ double acceptor charge state. Furthermore, uniaxial stress measurements have confirmed this interpretation.[8]

In GaAs crystals doped with nickel, an absorption band with a ZPL at 0.572 eV has been observed in all n-type samples[6,9] and has been tentatively attributed to Ni^+,[6] but a definitive assignment was not possible.[1,6]

This paper reports on optical absorption experiments of GaAs:Ni under uniaxial stress and magnetic field which prove unambiguously that the 0.572-eV ZPL arises from the $\Gamma_7(^2T_2)\rightarrow\Gamma_8(^2E)$ internal transition of the $Ni^+(3d^9)$ charge state of substitutional nickel and consequently that nickel is a double acceptor in GaAs.

The paper is divided in three main sections; the first presents the preparation of the samples and the experimental setup, then the uniaxial stress and Zeeman results are described, and the last section is devoted to discussion.

II. EXPERIMENTAL SETUP

A. Sample preparation

Selenium-doped n-type GaAs single crystals with free-electron concentration n of 7×10^{17} and 3×10^{18} cm^{-3} were used. Nickel was introduced by evaporating a layer of metal onto a slice of the semiconductor and then diffusing it during 24—50 h at high temperature (1000—1080 °C). After diffusion the samples were still n type, but their free-electron concentration decreased, which indicates a compensation process. The samples were x-ray oriented, optically polished, and chemically etched. Typical sample dimensions were $2\times2\times7$ mm^3.

B. Piezoabsorption measurements

The spectra were measured with a Zeiss SPM-2 grating monochromator with a cooled PbS detector. The spectral slit width was equal to 1—2 cm^{-1}. The samples were immersed in liquid helium, which was pumped below the λ point to about 2 K. Uniaxial stress was applied parallel to the [111], [100], and [110] directions, the intensity of the transmitted light was detected for light polarization parallel and perpendicular to the stress directions. In the case of the [110] stress, two different, nonequivalent configurations for the light beam parallel to the $[1\bar{1}0]$ and [001] directions were measured.

C. Zeeman measurements

The spectra were measured with a Jobin-Yvon HRS monochromator (with a resolution at about 0.2 cm^{-1}) and

an uncooled PbS detector. An Oxford Instruments optical cryostat with superconducting magnet allowing up to $B=6.4$ T magnetic field was used. The sample temperature was about 6 K. Faraday and Voigt configurations were measured for $\vec{B}||[111]$, [110], and [100] directions.

The measurements in Berlin were made with a 1-m Jarrel-Ash monochromator, an uncooled PbS detector, and an optical cryostat with superconducting magnet made by Oxford Instruments. The maximum field was $B=10$ T. The sample was cooled down to $T=1.5$ K. Nevertheless, the linewidth of the examinated sample (different source from those described above) was more than 2 cm^{-1} for all applied fields; so we used a resolution between 0.5 and 1 cm^{-1}.

III. EXPERIMENTAL RESULTS

A. Absorption spectrum

The absorption spectrum of the n-type GaAs:Ni in the (0.53—0.61)-eV region is shown in Fig. 1. One can see the most prominent absorption line at 4615 cm^{-1} (vacuum wave number) with half width equal to about 2 cm^{-1} as well as some weaker lines at 4408 and 4697 cm^{-1}. These weaker features were observed and identified by Ennen *et al.*[10] The 4615-cm^{-1} line, observed independently of the donor species was interpreted as an intracenter transition within the $3d$ shell of the isolated nickel impurity, the 4408- and 4697-cm^{-1} lines were assigned to Ni-Se and Ni-Si complexes, respectively.

B. Piezoabsorption spectra

Some preliminary uniaxial stress measurements have been previously described.[11] For all directions of the applied stress the 4615-cm^{-1} line splits into two components. Typical spectra for different stress and polarization geometries are shown in Fig. 2. Note that for [110] stress the intensities of the 4615-cm^{-1} absorption line components depend on the light polarization and also on the direction of the light propagation vector. To obtain the value of the splitting as a function of applied stress the spectra for all stress directions were fitted with Gaussian shapes (dashed lines in Fig. 2). The splittings vary linearly with applied stress (Fig. 3) and the obtained stress coefficients are 0.7×10^{-8}, 1.2×10^{-8}, and 1.3×10^{-8} $cm^{-1}(N/m^2)^{-1}$ for [100], [110], and [111] stress directions, respectively. A significant shift of the center of gravity of the 4615-cm^{-1} line as a function of stress was also observed (Fig. 3) and is found to be $6.1\pm0.4\times10^{-8}$ $cm^{-1}(N/m^2)^{-1}$. This relatively large value of the isotropic shift, in comparison with the values of the splittings (about 1 order of magnitude greater) is in our opinion the main reason for the observed large broadening of the 4615-cm^{-1} line under stress (Fig. 2). This broadening probably due to some inhomogeneity of the stress in the sample prevented measurements for stresses higher than 3×10^8 N/m^2. It should be noted that in previous measurements on GaAs:Co^{2+} (Ref. 12) with the same stress

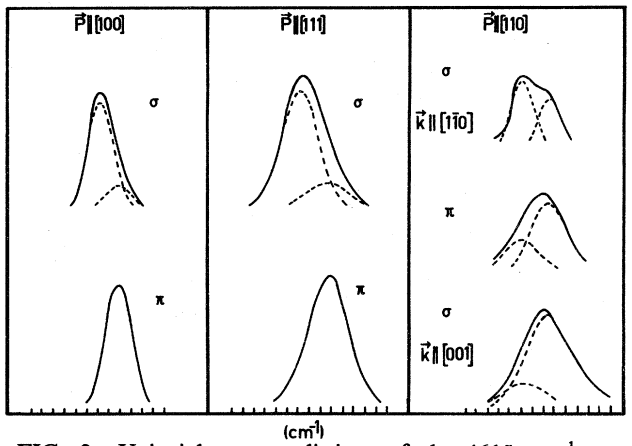

FIG. 2. Uniaxial stress splittings of the 4615-cm^{-1} zero-phonon line at 2 K for different stress directions and light polarizations ($P=2\times10^8$ N/m^2).

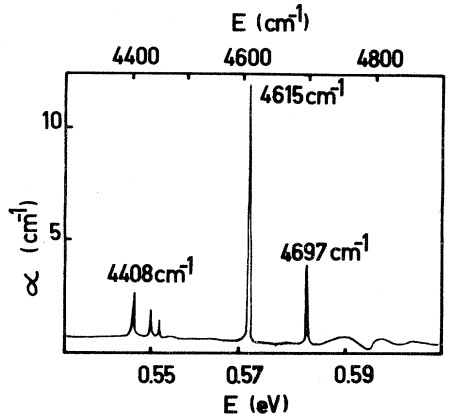

FIG. 1. Absorption spectrum of n-type GaAs:Ni at 2 K.

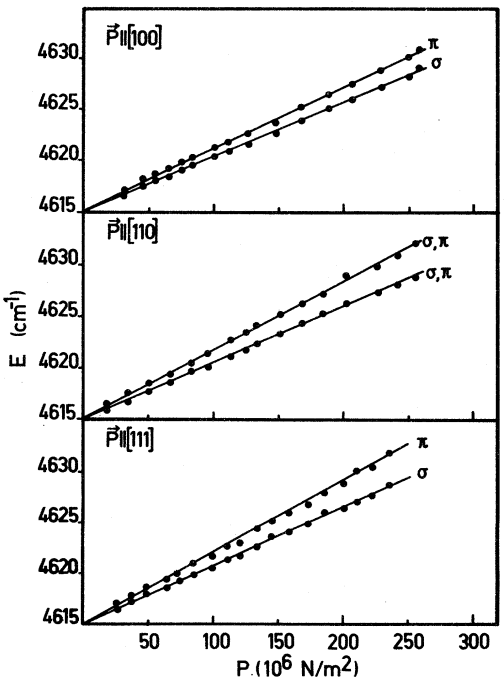

FIG. 3. Stress dependence of the 4615-cm^{-1} zero-phonon-line splitting for different stress directions.

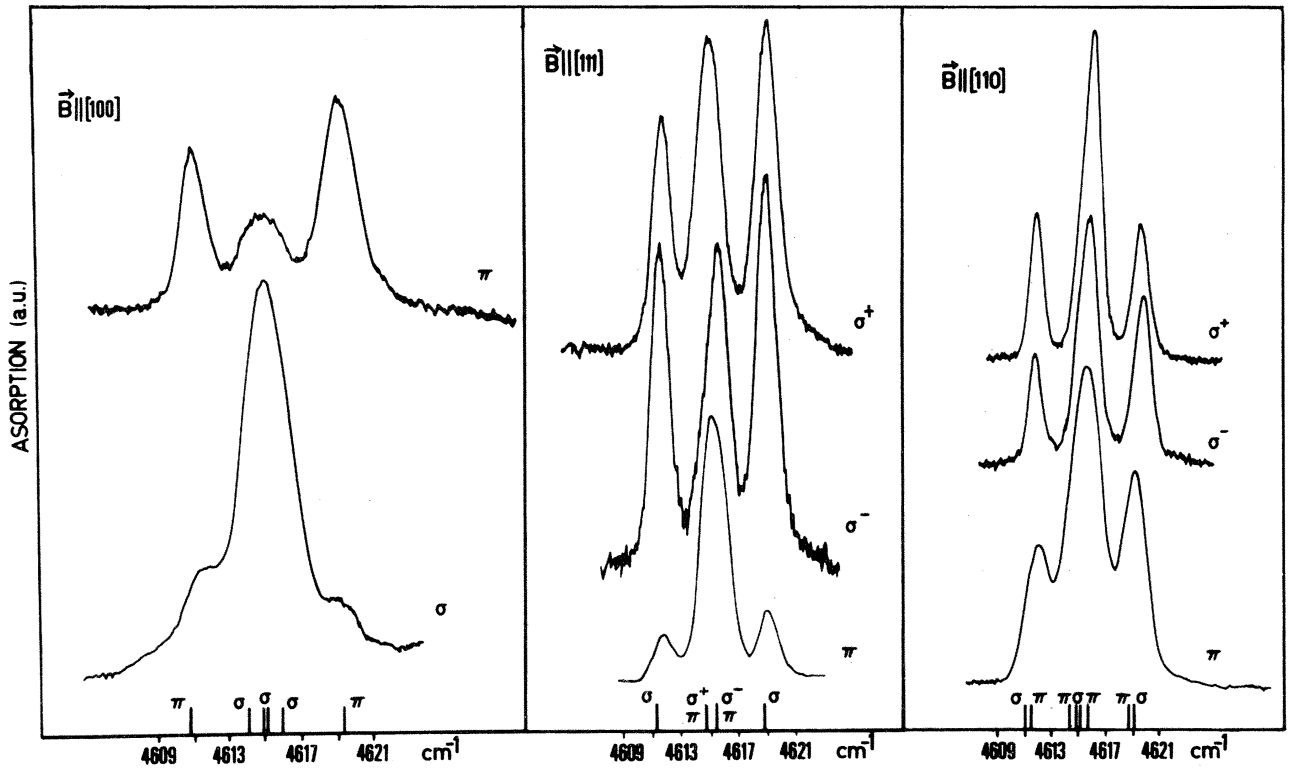

FIG. 4. Zeeman patterns of the 4615-cm^{-1} zero-phonon line for various polarizations and orientations ($B=6.4$ T, $T=6$ K). The stick diagram shows the calculated splittings and the selection rules for electric dipole transitions.

system, such a problem did not occur because the splitting of the Co^{2+} zero-phonon line and its isotropic shift were of the same order of magnitude.

C. Zeeman spectra

The obtained Zeeman spectra of the 4615-cm^{-1} absorption line at 6 K for π, σ^+, and σ^- polarizations are presented in Fig. 4, for a magnetic field of $B=6.4$ T parallel to the directions [100], [111], and [110], respectively. For the [111] magnetic field direction, the 4615-cm^{-1} line is seen to split into four components. The magnetic field dependence of this splitting is shown in Fig. 5. At a temperature of 1.5 K the dashed components disappear for B larger than 7 T. For $B||[110]$ one can observe five components and three for $B||[100]$. The obtained Zeeman splittings are anisotropic.

IV. DISCUSSION

A. Identification of the charge state of nickel impurity

The reported experiments allow the identification of the nickel charge state. $Ni^{2+}(3d^8)$ has to be rejected because its ground state should be a singlet which cannot be split by any magnetic field in contradiction with our results. Furthermore, Ni^{2+} cannot account for the [110] uniaxial stress splitting.[8]

The attribution of the 4615-cm^{-1} ZPL line to the $\Gamma_7(^2T_2)\rightarrow\Gamma_8(^2E)$ intracenter transition of $Ni^+(3d^9)$ is in good agreement with our results: In accordance with Table I, the ground state (Γ_7) splits under magnetic field but not under stress and the excited state splits under the influence of stress or magnetic field as a Γ_8 level should. It is to be noted that the excited-state splittings follow the well-known relation[13]

$$\Delta^2_{100}+3\Delta^2_{111}=4\Delta^2_{110}\,,$$

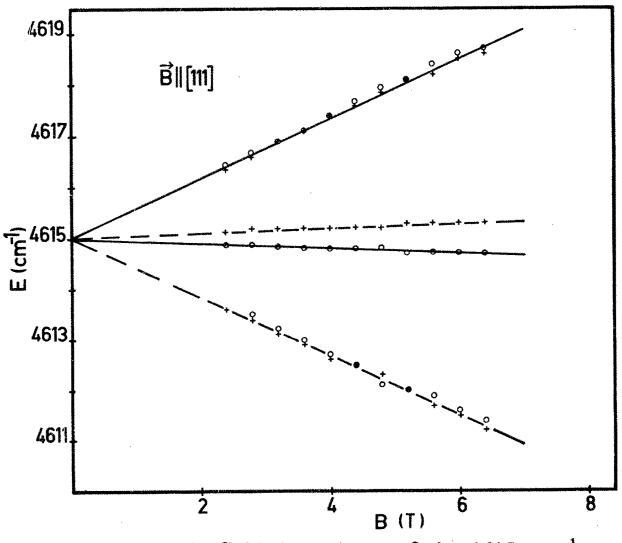

FIG. 5. Magnetic field dependence of the 4615-cm^{-1} zero-phonon-line splitting for $\vec{B}||[111]$. The dashed lines correspond to hot components. ($\circ,\sigma^+$; $+,\sigma^-$.)

TABLE I. Symmetry lowering of Γ_7 and Γ_8 levels under external stress and magnetic field.

Perturbation	Point-symmetry group	Ground state	Excited state
	$\bar{T}_d$	Γ_7	Γ_8
$\vec{P}\|\|[100]$	$\bar{D}_{2d}$	Γ_7	$\Gamma_6+\Gamma_7$
$\vec{P}\|\|[110]$	$\bar{C}_{2v}$	Γ_5	$2\Gamma_5$
$\vec{P}\|\|[111]$	$\bar{C}_{3v}$	Γ_4	$\Gamma_4+\Gamma_{5+6}$
$\vec{B}\|\|[100]$	$\bar{S}_4$	$\Gamma_7+\Gamma_8$	$\Gamma_5+\Gamma_6+\Gamma_7+\Gamma_8$
$\vec{B}\|\|[110]$	$\bar{C}_s$	$\Gamma_3+\Gamma_4$	$2\Gamma_3+2\Gamma_4$
$\vec{B}\|\|[111]$	$\bar{C}_3$	$\Gamma_4+\Gamma_5$	$\Gamma_4+\Gamma_5+2\Gamma_6$

where Δ_{100}, Δ_{111}, and Δ_{110} are the splitting energies under uniaxial stress parallel to the [100], [111], and [110] directions, respectively. The selection rules are also satisfactorily satisfied: The uniaxial stress experiments are in full agreement with the analysis of Hayes *et al.*[8] and the Zeeman experiments in rough agreement with the analysis of Kaufmann *et al.*[5] The presence of weak forbidden lines can be explained by internal stresses in the samples which lower the symmetry of the nickel sites and consequently break the selection rules. Thus we attribute the 4615-cm^{-1} absorption line to the $\Gamma_7(^2T_2)\rightarrow\Gamma_8(^2E)$ intracenter transition of $Ni^+(3d^9)$.

B. Zeeman splitting and analysis of *g* factors

According to the discussion presented by Kaufmann *et al.*[5] for GaP:Ni^+ the Zeeman splitting of the $\Gamma_7(^2T_2)\rightarrow\Gamma_8(^2E)$ transition can be characterized by three parameters: an isotropic g_7 value for the Γ_7 ground state and two *g* factors for the Γ_8 excited state, an isotropic one g_1 and another one g_2 inducing an anisotropy. For GaAs:Ni^+ we find that $g_7=-1.16$, $g_1=1.31$, and $g_2=-0.29$ with an error estimate of 0.05. The signs of g_7 and g_2 are opposite to that of g_1. So, taking g_7 negative, as it is generally accepted in the literature, we have to take g_1 positive and g_2 negative. The *g* values quoted above were used to calculate the splittings presented in Fig. 4. It is to be noted that we did not observe the Ni^+ EPR spectrum. The reason is probably an internal strain effect which leads to very large inhomogeneous EPR linewidth.[14]

The ground-state *g* factor g_7 differs strongly from 2. The reason is probably the same as for other d^9 cases in tetrahedral symmetry such as ZnS:Cu^{2+} (Ref. 15) or GaP:Ni^+,[5] i.e., a vibronic coupling of the $^2T_2$ ground state to ϵ-type vibrational modes. Using the same analysis as in Refs. 5 and 15, we obtain a Huang-Rhys factor of $S=1.6$ for a phonon energy $\hbar\omega=260$ cm^{-1} and covalency reduction factors[5] $k_1=0.7$ and $k_2\lambda_2/\lambda_0=0.7$. The same analysis locates the $\Gamma_8(^2T_2)$ state at $\delta=73$ cm^{-1} above the ground state.

The interpretation of the excited state $\Gamma_8(^2E)$ is more puzzling. The conventional expression for g_1, $g_1=g_e-k_2\lambda_2/\Delta$ for GaAs:Ni^+, leads to a minimum g_1 value of 1.48, if we forget the reduction factors. This value is significantly larger than the experimental one. It has to be noted that the same situation occurs in the case of GaP:Ni^+. The above formula has been obtained supposing that the ground state ($^2T_2$) is described by only two spin-orbit levels $\Gamma_7(^2T_2)$ and $\Gamma_8(^2T_2)$. In fact this is not true; because of the coupling of the ground state to the ϵ mode of vibration, a set of vibronic levels originating from the electronic $^2T_2$ level exists and the effect of all these levels changes the above formula. An exact calculation is rather complicated and the diagonalization of very large matrices is needed, but in the case where Ham's[16] conditions are fulfilled in the ground state, i.e., Jahn-Teller energy large compared to the spin-orbit constant of the ground state, this calculation becomes very simple and we obtain

$$g_1=g_e-\frac{4\lambda}{\hbar\omega}e^{-S}K\left[S,\frac{\Delta}{\hbar\omega}\right],$$

$$g_2=-\frac{4\lambda}{\hbar\omega}e^{-S}K\left[S,\frac{\Delta}{\hbar\omega}\right],$$

where the *K* function is defined by[17]

$$K(x,y)=\sum_{n=0}^{\infty}\frac{x^n}{n!(y+n)},$$

so that $e^{-S}K(S,\Delta/\hbar\omega)$ is simply $F^{-1}(\Delta/\hbar\omega,S)$ Englman's function.[18] It is to be noted that λ,Δ and $K(S,\Delta/\hbar\omega)$ are negative. If $|\Delta|/\hbar\omega$ is an integer, $K(S,\Delta/\hbar\omega)$ diverges, but this case is statistically very unlikely, and level repulsions should avoid these quasi-degeneracies. If $|\Delta|/\hbar\omega$ is large compared to *S*, one can use the asymptotic expression of the *K* function[17] and obtain

$$g_1\rightarrow g_e-\frac{4\lambda}{\Delta}\left[1-\frac{S\hbar\omega}{\Delta}\right]\simeq g_e-\frac{4\lambda}{\Delta+S\hbar\omega},$$

$$g_2\rightarrow-\frac{4\lambda}{\Delta}\left[1-\frac{S\hbar\omega}{\Delta}\right]\simeq-\frac{4\lambda}{\Delta+S\hbar\omega}.$$

Equivalent results can be obtained by the use of the Englman's effective denominator rule.[18] We can see that the introduction of all the vibronic levels arising from the ground state has a tendency to reduce the discrepancy with the experimental g_1 values. For instance, in GaP:Ni^+, where Ham's conditions are nearly fulfilled, the

lower g_1 value becomes 1.49 instead of 1.55, but the correction is not sufficient in order to get a satisfactory agreement between theory and the experimental value, which is 1.45. These low g_1 values are still slightly puzzling.

V. CONCLUSION

Our uniaxial stress and Zeeman experiments clearly show that the absorption spectrum characterized by the 4615-cm^{-1} ZPL in GaAs is due to Ni^+ double acceptor charge state of nickel. To our knowledge the identification of a stable double acceptor level in the GaAs energy gap had not been reported before.

An important problem is the location of the associated level within the band gap. In our samples, we observe a photoionization band having a threshold at 0.62 eV, but we do not have any evidence that this band is related to isolated nickel and one has to be careful before assigning it as has been shown in recent work on GaP:Ni.[19] We would like to mention that we do not observe any luminescence associated with the 4615-cm^{-1} absorption, whence we observe strong luminescences of the Ni-Se and Ni-Si complexes. This might mean that the Ni^+ excited state is above the conduction band. In such a case, the energy difference between the conduction band and the Ni^{2+}/Ni^+ level should be less than 0.57 eV.

One should remember that Partin *et al.*[20] did investigate the possibility for nickel to be a double acceptor in GaAs. They rejected this possibility because they had shown that the level they suspected to be the first acceptor level ($E_v+0.39$ eV) and the nickel-related level at $E_c-0.39$ eV could not be attributed to different charge states of the same center. Since Kumar and Ledebo[21] have demonstrated that the level at $E_v+0.39$ eV is not due to nickel but to copper contamination and therefore the possibility for the level at $E_c-0.39$ eV to be the double acceptor level of isolated substitutional nickel in GaAs still remains.

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