Interacting donors in n-type GaP studied with Raman scattering and ESR techniques

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Raman scattering and electron-spin-resonance (ESR) experiments have been performed on the same set of sulfur- and tellurium-doped gallium phosphide samples having various dopant concentrations. Impurity-related features of both Raman and ESR spectra indicate the presence of interactions between donors. The analysis of the data shows that these interactions are detected by Raman spectroscopy at a value of the mean distance between impurities significantly lower than that detected by the ESR technique.

I. INTRODUCTION

Sulfur and tellurium impurities in GaP have been studied by numerous workers and Carter *et al.*[1] reviewed the main results. In Raman spectroscopy, S and Te impurities give rise to bound phonons, as reported by Dean *et al.*[2] These phonons have also been studied by infrared spectroscopy by Barker[3] and more recently new structures have been observed in the Raman spectra.[4,5] ESR studies on these systems have been discussed by Title.[6] None of them are reported as a function of the concentration of donors to follow the evolution of the related features. This is an important point since, as this was extensively reported in the literature on n-type doped silicon, in the range of standard doping for GaP we expect significant effects due to interactions between donors.[7] This paper presents a systematic study of both Raman and ESR spectra taken on the same set of carefully characterized GaP:S and GaP:Te. Our objective was to study correlations between the Raman and ESR results. We report the observation of the delocalization of electrons bound to donors and pairing effects of impurities.

After a brief description of the experimental setup and the results on the characterization of samples, we describe first the properties of S-doped samples where the results are better understood and we extend the analysis of these data to interpret those obtained on GaP:Te. The analysis of the results gives parameters characterizing the interaction between impurities, parameters which will be compared, in the last section, to those reported in n-type silicon for equivalent ranges of concentrations. The discussion will emphasize differences in critical distances for which interaction between impurities appears in Raman and ESR techniques.

II. EXPERIMENTAL PROCEDURE

The Raman experiments have been performed with a Dilor RTI 30 triple additive monochromator with a resolution of 0.5 cm^{-1}. Because of the the large binding energies of sulfur and tellurium impurities in GaP these are in their neutral donor state at liquid-nitrogen temperature. This temperature is then sufficient to observe the bound phonons and all results are reported at 80 K for these experiments. Three different laser lines, 647.1 nm (Kr^+), 514.5 nm (Ar^+), 488 nm (Ar^+), have been used and no dependence of the effects reported here have been noticed. The results presented are those obtained with the 514.5-nm line.

The electron-spin-resonance experiments have been performed at $T \simeq 4$ K using an ER-200 Bruker spectrometer and an ESR-9 Oxford Instruments cryostat.

The samples come from different origins. The GaP:S samples have all been doped during growth whereas one of the GaP:Te samples has been doped during a liquid-epitaxy process. A variety of characterization procedures have been applied to the samples:

(i) Stark source mass spectroscopy (SSMS) and secondary-ion mass spectroscopy (SIMS) have been used to measure the concentration of impurities and their nature. For S-doped samples the residual impurity concentration is typically 2 orders of magnitude lower than the S concentration. It is not so for Te-doped samples, where in some cases non-negligible concentrations of S impurities have been detected. The results that we present here are for GaP:Te samples with S concentration at least 1 order of magnitude lower.

(ii) The concentration of free carriers has been measured by Hall-effect measurements as a function of temperature and also deduced from measurements of plasmon energy at high temperatures. From a standard analysis with a low compensation rate and single species of impurity, it is possible to deduce the concentration of impurities and compare it to the SSMS and SIMS results.

All techniques give results, for the donor concentration, which agree within ±30% for each sample. Table I reproduces the list of samples we used in the experiments together with the mean value of the concentration of impurities, n, as deduced by the different techniques. We also report for each sample the value of the reduced ra-

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TABLE I. Mean values of the impurity concentration n and the reduced radius $\bar{r}$ for the GaP:S and GaP:Te samples.

	GaP:S						
	$S1$	$S2$	$S3$	$S4$	$S5$	$S6$	$S7$
n (cm^{-3})	4×10^{17}	7×10^{17}	8×10^{17}	1.2×10^{18}	3.5×10^{18}	4.8×10^{18}	6.4×10^{18}
$\bar{r}$	13.6	11.3	10.8	9.4	6.6	5.9	5.4
	GaP:Te						
		$T1$	$T2$	$T3$	$T4$	$T5$	
n (cm^{-3})		1.5×10^{17}	1.9×10^{17}	2.3×10^{17}	4.6×10^{17}	8.9×10^{17}	
$\bar{r}$		16.2	14.9	14.1	11.2	8.9	

dius $\bar{r}$, which will be defined in Sec. V.

The range of concentrations for Te-doped samples is not very wide and we will first analyze the results obtained on S-doped samples, where the effect of increased doping is more pronounced.

III. RESULTS ON GaP:S

A. Raman results

Bound phonons appear as structures on the low-energy tail of the LO modes in polar crystals. The corresponding spectra for four different GaP:S samples are displayed in Fig. 1. They have been intentionally enlarged to show the low-energy details of the spectra. All experiments have been performed in a backward geometry, which is not essential because the polarization selection rules are found to be the same for both the LO line and the low-energy sidebands in accordance with the results of Dean *et al.*[2]

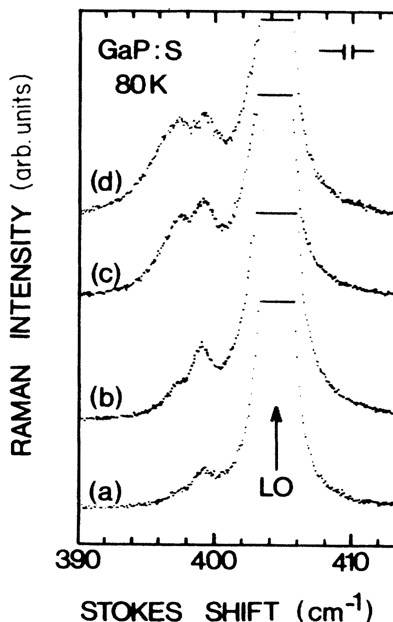

FIG. 1. Raman spectra for different S-doped GaP samples at 80 K: (a) sample $S1$; (b) sample $S4$; (c) sample $S6$; (d) sample $S7$. The origin for vertical scale has been shifted from one spectrum to the other. The spectral resolution is sketched on the right upper part of the figure.

The same typical spectra which exhibit two sidebands have also been reported by Bairamov *et al.*,[4] but with a resolution 2 or 3 times lower than ours ($\Delta\omega=0.5$ cm^{-1} at $\omega\simeq20000$ cm^{-1}). Because of this good resolution, we could determine that the two main features do not behave proportionally to impurity concentration. As the S concentration increases, an asymmetry develops on the low-energy side of the LO line and becomes important for highly doped samples.

A quantitative description requires the evaluation of the integrated intensities of the different features. In order to do that, we have deconvoluted the spectra in two successive steps, illustrated in Fig. 2: The increasing asymmetry on the low-energy side of the LO phonon is likely to be due to the impurity-induced disorder and could be well reproduced by a spatial correlation model of the kind proposed by Parayanthal and Pollak.[8] Note that the model of Ref. 8 does not depend on the exact physical nature of the disorder and results in an asymmetric Lorentzian curve. The first step is then to fit such a curve to the observed LO line [Fig. 2(a)] and subtract it from the experimental spectrum. The remaining part of the spectrum is clearly

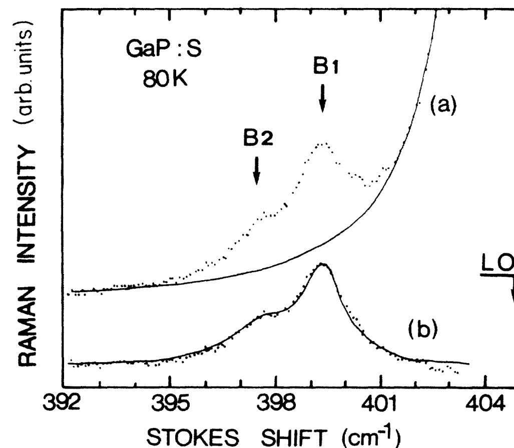

FIG. 2. Deconvolution of the Raman spectrum for sample $S4$. (a) The solid line is a fit of an asymmetric Lorentzian to the LO line. (b) Dots are the result of the subtraction from the spectrum of the asymmetric Lorentzian determined in (a). The solid line is the result of the fit of two Lorentzian bands to this subtracted spectrum.

composed of two bands, $B1$ and $B2$, representative of bound phonons [Fig. 2(b)] which have to be further deconvoluted. At low concentrations it is natural to assign the bound phonon which is clearly dominant (band $B1$) to the isolated S impurity. Its line shape is well reproduced by a Lorentzian which, when subtracted, gives the second band, $B2$. The latter can be fitted either with a Gaussian or a Lorentzian within the experimental error. The position of the maximum of $B2$ as well as its integrated intensity do not depend significantly on the nature of the fitting curve. In practice, it has been fitted to a Lorentzian. All our spectra have been deconvoluted this way: it results in a structure related to the known bound phonon $B1$ with a binding energy (with respect to the LO energy) $E_B = 5.4 \pm 0.1$ cm^{-1}. The second structure, $B2$, peaks at $E_B = 7.3 \pm 0.2$ cm^{-1}. Both binding energies are found to be concentration independent.

As previously reported,[5] when the normalized integrated intensities of $B1$ and $B2$ with respect to the integrated intensity of the LO line are plotted as a function of the *total* number of impurities, n, the dependence of the intensity of $B1$ is linear, whereas that of $B2$ is quadratic. This leads us to assign $B2$ to phonons bound to sulfur complexes which are mainly pairs in that range of concentration. The qualitative arguments are (i) this phonon is related to a S impurity since it does not exist in samples with other dopants, and (ii) it cannot be assigned to an isolated impurity because its intensity should then follow that of the other phonon, $B1$, which is clearly not the case. This is in contradiction with the interpretation of Bairamov *et al.*,[4] who assign $B2$ to the bound phonon related to the $1s$-$2p_0$ transition and $B1$ to the $1s$-$2p_\pm$ transition. Beside the fact that there is, to our knowledge, no unambiguous experimental proof that the response function related to bound phonons for a single impurity is composed of more than one structure, the intensity analysis by itself rules out, in this case, the interpretation of Bairamov *et al.*[4] Furthermore, we show in Fig. 3 a comparison between the full width at half maximum (FWHM) for both structures as a function of impurity concentration. Whereas the width related to $B1$ is constant, of the order of 1.3 ± 0.1 cm^{-1}, $B2$ has a width increasing from 1.3 to 3.5 ± 0.3 cm^{-1}. This probably indicates the statistical repartition of distances between atoms of a pair.

A more precise intensity analysis can be done as a function of the number of different entities. If we assume that the interaction between two impurities becomes noticeable when they enter a given volume v, the probability of finding N sulfur atoms in this volume is given by the Poisson distribution[9]

$$P_N = \frac{(nv)^N}{N!} e^{-nv} , \tag{1}$$

where n is the total concentration of donors.

We can then deduce the mean number of isolated impurities, $n_1 = P_1/v$, and of the pairs, $n_2 = P_2/v$. The parameter v is fitted in such a way that the intensities of the phonons bound to isolated and paired impurities are linear functions of n_1 and n_2, respectively. This is displayed in Fig. 4. The fitted volume v_S corresponds to a radius of 33 ± 2 Å, equal to about 5.3 Bohr radii of the S impurity. This is in accordance with the results on the binding of the hydrogen molecule[7] and will be discussed in the last section.

We found that the ratio of the Raman cross sections is 10 times higher for a pair than for a single impurity. This factor cannot be directly related to the ratio of the pair polarizability and that of an isolated impurity since the intensity of bound phonons is proportional to the volume where the electronic polarizability changes. This volume depends significantly on the chemical shift suffered by the isolated impurity, a correction which is expected to be less important for the pair. It is likely that the ratio of these polarizabilities be smaller than 10.

The optical absorption due to interacting donors in Si:P has been investigated by Thomas *et al.*[7] These authors found in this case that the strongest transitions $1s \rightarrow 2p_0, 2p_\pm$ of the isolated donor are replaced by broader transitions $D_{1s} - D_{2p_0}, D_{2p_\pm}$ of a hydrogenlike molecule at a *lower* energy than the corresponding isolated donor transition energies. Following the theory of Dean

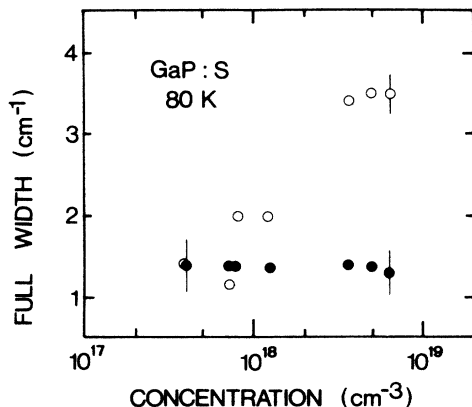

FIG. 3. Full width at half maximum of the two bound phonons in GaP:S; solid and open circles correspond, respectively, to the bound phonons with the lowest and highest binding energy.

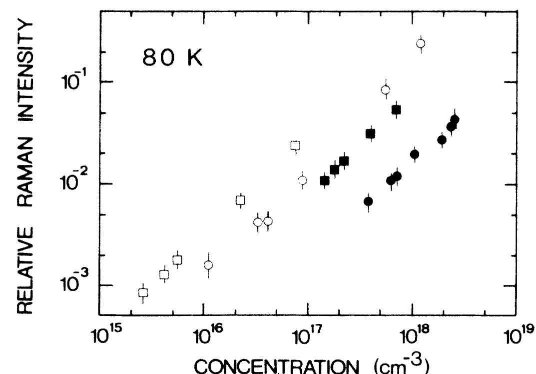

FIG. 4. Relative integrated Raman intensities with respect to the integrated intensity of the LO line as a function of the number of isolated impurities (solid symbols) and the number of paired impurities (open symbols). Circles are for GaP:S samples and squares for the GaP:Te samples.

et al.,[2] this would correspond to a larger binding energy for the corresponding bound phonon, in agreement with our experimental results. The doping level at which pairs of donors are observed in Si is about 3×10^{16} cm^{-3}, but is expected to be an order of magnitude higher in GaP since the Bohr radius a_0 for S is about 3 times lower than that of an As or P impurity in Si and the scaling involves the quantity $n^{-1/3}a_0$.

In conclusion, it is very likely that the new bound phonon which appears in GaP:S samples is related to the pairing and complex of S impurities.

B. ESR results

All the GaP:S samples have been investigated by the ESR technique. The ESR spectra are characterized by a strong and broad central line, since the large majority of the S atoms have a zero nuclear spin and the donor wave function extends over a large number of Ga and P neighbors. The hyperfine structure which would correspond to the isotope ^{33}S (natural abundance 0.76%) with the nuclear spin $\frac{3}{2}$ is not observed. The resonance magnetic field B_0 at 9.46 GHz corresponds to a g value of 1.99. This agrees with the results of Title.[6] The derivative of the central line with respect to the magnetic field is displayed in Fig. 5. We show the half part of the derivative of the lines normalized to unity at high magnetic field for increasing concentration of S impurities.

The FWHM of the ESR line decreases from 120 G (sample $S1$) to 84 G (sample $S7$). The shape changes by itself: for low concentrations, the donor wave function extends over the neighboring Ga and P nuclei and, since the individual lines are not resolved, a Gaussian line shape should be observed.[10] This is not true even for the sample $S1$. Also, as the concentration increases the line narrows significantly (Fig. 5). Note the abrupt change of the line shape between samples $S4$ and $S5$. The narrowing of the ESR line with increasing concentration has already been observed in Si:P by Maekawa and Kinoshita.[11] In their analysis of the ESR central line, they observe in the doping range from 7×10^{17} to 3×10^{18} cm^{-3} a significant narrowing of the line with a Lorentzian shape. This shape can account for the ESR signals for samples $S5$, $S6$, and $S7$ shown in Fig. 5.

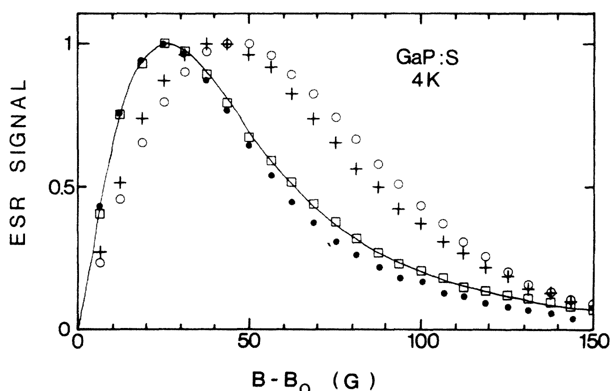

FIG. 5. Comparison between the line shapes of the ESR-derived signal for GaP:S: Open circles, sample $S1$; crosses, sample $S4$; open squares, sample $S5$; solid dots, sample $S6$. The maximum of all signals has been normalized to unity. Solid line is a Lorentzian curve fitted to the ESR signal for sample $S5$.

For lower concentrations the line shape we observe is intermediate between Lorentzian and Gaussian. For Si, the central line was attributed to the effect of interaction between donors alone, whereas in GaP an important contribution to the line originates from the hyperfine interaction of the impurity with neighboring atoms, at least for lower doping levels. These interactions between impurities become dominant in GaP at donor concentrations which agree with donor concentration in Si appropriately scaled by the ratio of impurity Bohr radii. In the present case, a quantitative analysis would require a deconvolution of the central line which would yield large uncertainties. Therefore we constrain the discussion to a qualitative comparison. The interpretation of the line narrowing proposed by Maekawa and Kinoshita[11] involves both exchange interaction between donors and hopping motion of electrons. This has been explained by the Anderson-Weiss theory.[12] We cannot, unfortunately, apply this theory in our case since the intrinsic width and shape of the line due to hyperfine interaction are not known. It is clear, however, that the ESR experiments confirm that for n ranging from 4×10^{17} to 6×10^{18} cm^{-3}, the exchange interactions between impurities become important. These should lead statistically to the presence of paired impurities, as this is seen in Raman experiments.

IV. RESULTS ON GaP:Te

A. Raman results

In GaP:Te bound phonons appear as a single sideband on the low-energy tail of the LO line. Within the experiment resolution no other additional structure than that displayed in Fig. 6 has been detected. The Raman spectra for GaP:Te have been deconvoluted in the same way as

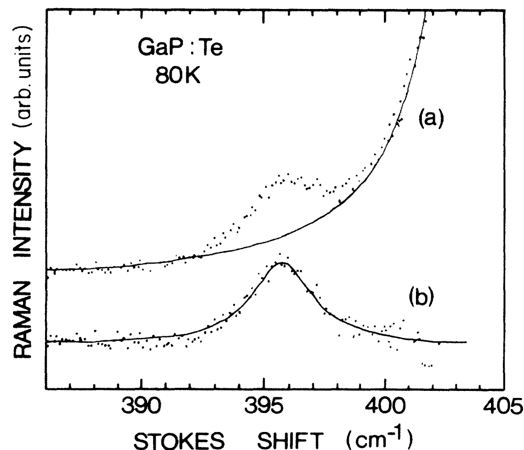

FIG. 6. Deconvolution of the Raman spectrum for sample $T1$. (a) The solid line is a fit of an asymmetric Lorentzian to the LO line. (b) Dots are the result of the subtraction from the spectrum of the asymmetric Lorentzian determined in (a). The solid line is a Lorentzian curve fitted to the deconvoluted structure.

for GaP:S. A Lorentzian can be fitted to the observed sideband. It corresponds to a binding energy of 9 ± 0.3 cm^{-1} with a FWHM of 4.4 ± 0.4 cm^{-1}. These quantities are found to be independent of the impurity concentration. The increase in the binding energy of the bound phonon $B1$, from 5.4 cm^{-1} (GaP:S) to 9 cm^{-1} (GaP:Te), is well accounted for by theory[2] since the transitions inside the sublevels of the Te impurity are at lower energies than those corresponding to S. Note, however, that the width is significantly larger than that obtained even for phonons bound to pairs in GaP:S. The difference in binding energies between Te and S impurities is due to a larger chemical shift of the latter. However, the central-cell correction should not affect the electronic levels of pairs as much as those of the single impurity, since the wave function of pairs is not centered on the impurity site. We can therefore expect smaller differences between electronic structures of Te and S pairs, than that for individual impurities. Consequently, a phonon bound to a Te pair should appear at a binding energy close to that of a S pair. Since, furthermore, the threshold for the pairing should be lower for Te than for S impurities, due to a larger Bohr radius a_0 of the former, it is not clear, *a priori*, whether the observed sideband should be related to single impurity, to pairs, or both.

If we follow the same statistical analysis that we performed for S-doped samples, we can calculate mean values for n_1 (isolated impurities) and n_2 (pairs), assuming that the volumes v_{Te} and v_S scale as a_0^3. This volume corresponds to a radius of about 38 Å. When the total relative intensity of the sideband is plotted as a function of n_1, the resulting slope is higher than 1 but smaller than 2, whereas it is lower than 1 when plotted as a function of n_2. This indicates that the broad experimental structure is a mixture of both types of bound phonons. If it is correct, it should be possible—using as a fitting parameter the ratio of the Raman cross sections between the two phonons—to divide the total intensity into two parts, each of them being proportional to the concentration of the related entity. This is obtained with a ratio $I_{pair}/I_{single}\simeq 4$ (see Fig. 4). This ratio is not very sensitive to the value of v_{Te} within a reasonable range of scaling. It is lower than the ratio found for GaP:S. This was expected because of the smaller chemical shift suffered by Te impurity.

In conclusion, the value of the binding energy equal to 9 cm^{-1} should be understood as a mean value between that of the isolated impurity bound phonon and that of the pair in GaP:Te samples.

B. ESR results

The ESR spectrum of the more lightly doped GaP:Te sample ($T1$) is shown in Fig. 7. As in the case of the S impurity, the main central line corresponds to $g=1.99$. However, for this sample at quite lower sensitivity, two pairs of symmetrical lines appear which could be attributed to hyperfine interaction for the two Te isotopes which have a nuclear spin $I=\frac{1}{2}$ of ^{123}Te (natural abundance 0.87%) and of ^{125}Te (natural abundance 6.99%). This fact is interesting, since, to our knowledge, this hyperfine structure has never been observed in chalcogenide-doped GaP. In more heavily doped samples ($T2\rightarrow T5$) this interaction is absent, as in Si:P (Ref. 11), due to the onset of exchange interaction between neighboring donors. We can determine the isotropic hyperfine constant A for both isotopes,

$$|A|=(1110\pm10)\times10^{-4}\ cm^{-1}\ \text{for}\ ^{125}\text{Te}\ ,$$

$$|A|=(870\pm10)\times10^{-4}\ cm^{-1}\ \text{for}\ ^{123}\text{Te}\ .$$

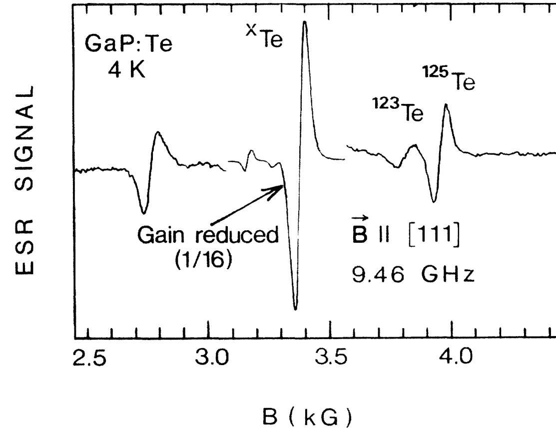

FIG. 7. ESR of the ground state of the Te donor in GaP (sample $T1$). ^{x}Te denotes the contribution of even Te isotopes with zero nuclear spin, whereas structures corresponding to ^{123}Te and ^{125}Te are seen. The signal around 3.2 kG is related to Fe^{+}.

Their ratio equal to about 1.27 is well accounted for by the ratio of the nuclear magnetic moment for ^{125}Te and ^{123}Te (4.71/3.90=1.21). In principle, the relative intensities of the lines should correspond to the relative natural abundance of the Te isotopes. The strong central line arises from the Te isotopes with zero nuclear spin as observed in GaP:S. We measure a peak-to-peak linewidth of 45 G for the Zeeman line and of 50 G for the hyperfine lines. The relative integrated intensity of the ^{123}Te and ^{125}Te lines is found to be lower than expected: For instance, for ^{125}Te we find the value between 5.5% and 6% to be compared with 7% following from the natural abundance of the isotope. This little discrepancy which may be due to a slight lattice strain can, in addition, originate from different sources:

(i) The SSMS analysis always gives for Te-doped samples a concentration of S which is not completely negligible at the sensitivity of the ESR technique (they are not seen in Raman spectra). Since the central line for Te and S occurs at the same g value, the presence of S impurities would increase the intensity of the central line.

(ii) Another explanation is that, already in that range of concentrations, the exchange interaction between donors is appreciable; it leads, according to the results[11] on Si:P, to a decrease of the hyperfine interaction and an increase of the ESR contribution of the central line. In both cases, we do not expect that the central line would be Gaussian, which is, in fact, not observed.

The measured hyperfine constant A is approximately the same as that reported for Si:Te^{+} by Grimmeiss

et al.[13] We can then have an estimate of the probability of finding an electron on the donor site, $|\psi(0)|^2$, using the standard relation

$$A=(8\pi/3)g_e\mu_e g_n\mu_n\,|\psi(0)|^2\,, \quad (2)$$

where g is the Landé factor and μ the Bohr magneton for, respectively, the electron (e) and the nucleus (n). If we compare $|\psi(0)|^2$ to that of the free atom, $|\psi_A|^2$, as defined by Grimmeiss *et al.*,[13] we obtain $|\psi(0)|^2/|\psi_A|^2\simeq 0.1$. Therefore, as in Si, the probability of finding an electron on the donor center is about 0.1.

As n increases, the hyperfine structure disappears, and the central line narrows. The FWHM is found to decrease from 74 G ($T1$) to 66 G ($T5$) and the line is never Lorentzian even for sample $T5$. Note that this decrease is less pronounced than for GaP:S. This may be due to the fact that the intrinsic width of the central line related to the isolated donor is appreciably smaller for Te than for S. This difference in the intrinsic width should reflect the different extension of the $1s$ wave function for S and Te. For larger a_0, the electron will overlap more distant neighbors, and the hyperfine interaction with them, being weaker, will contribute essentially to the center of the main line and make it sharper.

Within the range of concentrations we investigate, we do not reach, even for the highest doping, a point where the exchange interaction between donors dominates as it was the case of GaP:S. Actually, estimated values of n_1 and n_2 indicate that the sample $T5$ should correspond to an intermediate situation between $S4$ and $S5$ samples in a region where the ESR line shape, as already noticed, changes from Gaussian to Lorentzian.

Even if not dominant, these interaction effects between donors are clearly present and justify our approach in interpretation of the Raman spectra of GaP:Te samples.

V. DISCUSSION OF THE RESULTS

We would now like to discuss our results and relate them to what is known on donor interactions in Si. The reason for which we choose this as a reference is because we expect the donor levels in silicon to have similar properties as those in GaP due to the similarity of the lowest conduction bands in both semiconductors. Of course, the values of a_0 are different in each case and the relevant parameter which should be used for comparison is the reduced parameter $\langle r\rangle/a_0=\bar{r}$, where $\langle r\rangle$ is the mean distance between donor impurities defined as $(n4\pi/3)^{-1/3}$. The parameter $\bar{r}$ is calculated for each sample and listed in Table I. The values of a_0 for S and Te are taken, respectively, as 6.2 and 7.2 Å. The ESR results on Si:P (Refs. 11 and 14) and Si:As (Ref. 15) have been discussed by Marko and Quirt[16] and Cullis and Marko.[17] These authors, following a method proposed by Jerome and Winter,[14] have calculated the exchange constant J_{ij} between two electronic spins as a function of the distance r_{ij} between donors, with appropriate wave functions for a donor in Si. They show that the interacting effects become dominant when this constant J_{ij} is of the order of the hyperfine constant A, which occurs for $\bar{r}\simeq 7$. Recently, New and Castner[18] performed a quantitative analysis of ESR spectra of donor clusters in silicon and again found a critical radius of about 7, below which clustering effects dominate. In GaP, as already pointed out, the essential hyperfine interaction is that with neighboring atoms. An estimate of its strength is given by the width of the Gaussian-like central line for weakly doped samples. The corresponding values are 120 G (336 MHz) for GaP:S and 80 G (224 MHz) for GaP:Te. The calculations of Cullis and Marko[17] can be scaled with the hyperfine constant and the a_0 to the case of GaP and lead to a value of J_{ij} of the order of 300 MHz for r_{ij} ranging between $6.9a_0$ and $7.1a_0$. This corresponds to the case (see Table I) intermediate between samples $S4$ and $S5$. It is important to notice that this is also the range where the line shape changes significantly from Gaussian-like to Lorentzian-like (Fig. 5). This change was not observed in GaP:Te since we did not investigate samples with $\bar{r}<7$. So it seems that this critical value of 7 for $\bar{r}$ is also characteristic of the ESR results on donor clusters in GaP. The exchange constant J_{ij} decreases quasiexponentially[16] with r_{ij}, which means that the difference for $\bar{r}$ between 7 (as deduced from ESR experiments) and 5.3 (as deduced from Raman experiments) is significant and cannot be explained by errors in the scaling of J_{ij}. Before discussing this point, it is instructive to analyze the effects which can give an electronic polarizability different from that of a single impurity.

In their absorption experiments on Si:P, Thomas *et al.*[7] clearly show that the interaction between donors induces two types of transitions related to $D_{1s}D_{2p_{0,\pm}}$ pairs and D^+D^- pairs. The latter occur at an energy lower than the former only for high doping level corresponding to $\bar{r}\lesssim 8$. Even in that case, the optical cross section is much lower for D^+D^- transitions than for the $D_{1s}D_{2p}$, at least as long as the upper and lower Hubbard bands D^- and D^+ are not present. This corresponds to a situation in the conduction process where the ϵ_2 mechanism appears.[19] There is, to our knowledge, no report on this latter effect in Si:P, but it has been seen[20] in Ge:Sb for a value of $\bar{r}$ of the order of 4. It is very likely that, in our case, this limit is not reached: the origin of the new electronic polarizability for complexes should then be mainly related to the $D_{1s}D_{2p}$ transitions. The Raman activity for $B2$ corresponds to the existence of pairs which exhibit a local polarizability quite different from the sum of local polarizabilities of individual neutral donors. This can happen only when the electronic wave function of the pair has a substantial amplitude in the interspace between donors, a situation which occurs at a distance lower than that for which atoms begin to interact and to induce some exchange interaction between electrons as seen in ESR experiments. Therefore we expect to observe interactions between donors at a value of the $\bar{r}$ parameter lower with the Raman technique than with the ESR one.

In conclusion, we think that both Raman and ESR results give evidence for interacting donors in n-type GaP at an impurity concentration of about 10^{17} cm^{-3}.

VI. CONCLUSION

The Raman as well as the ESR techniques applied to the study of GaP:S and GaP:Te at various concentrations show the existence of interaction processes between donors. A statistical analysis and a correlation with known results on *n*-type Si favors the idea that this interaction induces donor pairing. The characteristic distance below which the complexes give a specific signature in Raman scattering is found to be of the order of five Bohr radii of the isolated impurity. Work on the evaluation of the binding energy of phonons bound to these complexes is now in progress.

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