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Muonium centers in GaAs and GaP

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The authors present the first observation of muon spin rotation for normal (Mu) and anomalous (Mu*) muonium centers in compound semiconductors, specifically GaP and GaAs. As in the elemental semiconductors, the muonium defect centers are characterized by a large isotropic hyperfine interaction for Mu but by a small, highly anisotropic, ⟨111⟩ symmetric hyperfine interaction for Mu*. All hyperfine parameters measured in GaAs are remarkably close to those obtained in GaP. Furthermore, $|A_{\parallel}^{*}|$ is greater than $|A_{\perp}^{*}|$ for Mu*. These last results are in marked contrast with the observations in diamond, Si, and Ge.

Muonium is a hydrogenlike atom in which the proton is replaced by the lighter positive muon ($m_\mu \simeq m_p/9$). In contrast with the absence of EPR results on hydrogen in semiconductors, the technique of muon spin rotation (μSR) has provided a wealth of information on the electronic structure of muonium defect centers in the elemental semiconductors.[1,2] These centers can be characterized by the muon-electron hyperfine interaction which depends on the unpaired-electron spin-density distribution near the muon. In diamond, Si, and Ge two centers have been observed: a center called normal muonium (Mu) with an isotropic hyperfine constant of about half the free muonium value and a center called anomalous muonium (Mu*) with a small anisotropic hyperfine interaction with ⟨111⟩ symmetry. Theoretical studies[3-6] indicate that the Mu-crystal potential has a minimum at the tetrahedral interstitial site but that there is only a small potential barrier between adjacent sites. Experimental work[7] confirms that Mu is moving rapidly in the group-IV crystals. Although Mu* is less well understood several theoretical arguments[8-10] suggest that Mu* is a substitutional muonium atom rather than interstitial at the hexagonal site as proposed earlier.[11]

Little is known about muonium in compound semiconductors. In materials (such as GaAs and GaP) that contain a high percentage of nuclei with magnetic dipole moments, the μSR precession frequencies cannot be detected in low magnetic fields because of line broadening due to nuclear hyperfine (NHF) interaction.[12] Measurements of the muon polarization amplitude as a function of magnetic field (applied parallel to the incident muon polarization) indicate the presence of muonium centers in GaAs,[13] but a quantitative analysis of the centers requires the observation of the precession frequencies.

We report here the observations of Mu* and Mu precession frequencies in GaAs and GaP in a high transverse magnetic field (1.1 T) where the muon, electron, and nuclear spins are decoupled and thus line broadening due to NHF interaction is quenched. The observed hyperfine parameters are remarkably similar in GaAs and GaP for both types of centers. Furthermore the anisotropic hyperfine parameters for Mu* are such that $|A_{\parallel}^{*}| > |A_{\perp}^{*}|$. These results are quite different from those obtained in the elemental group-IV semiconductors.

The present observations are made possible by a recent technical advance[14] which allows us to observe muonium precession frequencies in a large transverse magnetic field. Details of the high-field (1.2 T) high-timing-resolution (200 ps) apparatus will be presented elsewhere.

During the experiment (performed at the Swiss Institute for Nuclear Research), spin-polarized muons of momentum 85–105 MeV/c were stopped in single crystals of undoped, low-resistivity GaAs and GaP obtained from Wacker Chemitronics in West Germany. The samples had room-temperature carrier concentrations of 4×10^{16} and 2×10^{16} cm^{-3}, respectively. Additional measurements were made on a single crystal of undoped, high-resistivity GaAs obtained from Hewlett-Packard, Palo Alto, California. The μSR spectra were taken over the temperature range 10–300 K while applying a large transverse magnetic field (0.3–1.3 T).

A μSR frequency spectrum for the high-resistivity GaAs with the field parallel to a ⟨110⟩ direction is shown in Fig. 1. The four low-frequency lines labeled ν_{ij}^{*} are attributed to a paramagnetic center with a small anisotropic hyperfine interaction that we call Mu*. These frequencies were observed in both the high- and low-resistivity GaAs. The dependence of the low-frequency lines upon the magnetic field is shown in Fig. 2 for a low-resistivity GaAs crystal with the field applied along a ⟨111⟩ direction. The dependence of these Mu* frequencies on magnetic field and crystal orientation is consistent with an anisotropic spin Hamiltonian axially symmetric about the ⟨111⟩ (or z) axis:

$$\mathscr{H}_{\mathrm{Mu}^*} = A_{\parallel}^{*} S_z^{\mu} S_z^{e} + A_{\perp}^{*}(S_x^{\mu} S_x^{e} + S_y^{\mu} S_y^{e}) + |g_e|\mu_B \mathbf{S}^e\cdot\mathbf{B} - |g_\mu|\mu_\mu \mathbf{S}^\mu\cdot\mathbf{B} \ , \qquad (1)$$

where the g factors are taken isotropic. In high transverse magnetic fields ($\mu_B B >> |A_{\parallel}^{*}|$ and $|A_{\perp}^{*}|$), we obtain from Eq. (1) two precession frequencies ν_{12}^{*} and ν_{34}^{*} for each value of θ, the angle between the ⟨111⟩ symmetry axis and the magnetic field direction. Therefore, with the field applied along a ⟨111⟩ (or a ⟨110⟩) direction, this leads to a

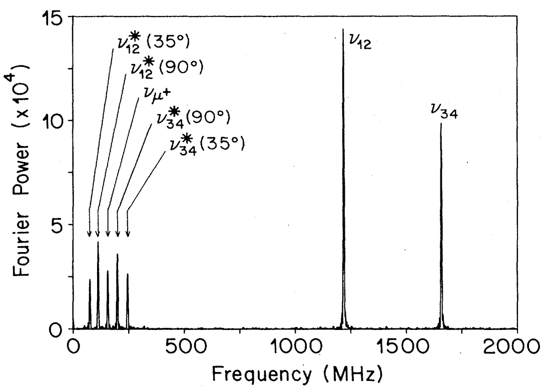

FIG. 1. Muon spin-frequency spectrum in high-resistvity GaAs at 10 K with a transverse magnetic field of 1.15 T applied along a ⟨110⟩ axis. The starred frequencies are due to anomalous muonium (Mu^*). The bare muon frequency (ν_{μ^+}) is due primarily to muons stopping in the cryostat. The high frequencies (ν_{12} and ν_{34}) result from normal isotropic muonium (Mu).

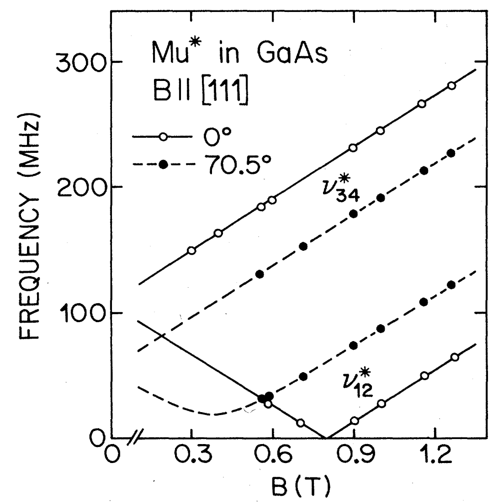

FIG. 2. Magnetic field dependence of the Mu^* frequencies in GaAs at 23 K. The frequencies depend on the angle θ between the ⟨111⟩ axis and the applied field. The solid and dashed curves are a fit to the theoretical spectrum for θ equal to 0° and 70.5°, respectively.

total of four precession frequencies: two from the centers characterized by $\theta = 0°$ (or 90°), and two from the centers with $\theta = 70.5°$ (or 35.3°). This is illustrated in Figs. 1 and 2. It is easy to show that the 0° and the 90° lines are far less sensitive to small misalignments of the crystals than the 70.5° and the 35.3° lines: consequently, the Mu^* hyperfine parameters listed in Table I are obtained by fitting the 0° and 90° lines with Eq. (1).

The Mu^* μSR signals in GaAs and GaP were not observable above 100 K or in magnetic fields smaller than 0.3 T because of a rapid increase in the depolarization (i.e., relaxation) rate. Details and conclusions on these measurements will be presented elsewhere.

The two highest frequencies in Fig. 1 (ν_{12} and ν_{34}) are attributed to Mu which has a large isotropic hyperfine interaction. The hyperfine interval is equal to the sum of these two frequencies.[14] Mu was observed in high-resistivity GaAs, but was not observed in low-resistivity GaAs, although there was no change in the Mu^* and in the bare muon precession amplitudes between the two samples. This indicates that Mu in low-resistivity GaAs is probably depolarized due to interaction with paramagnetic impurities.[19] Spectra similar to that shown in Fig. 1 were observed in low-resistivity GaP. However, the Mu depolarization rate in GaP at 10 K (100 μs^{-1} from Ref. 14) was 50 times larger than that in high-resistivity GaAs (2 μs^{-1}). In Table I the hyperfine parameters and formation probabilities for Mu and Mu^* in GaAs and GaP are compared with those in Si, Ge, and diamond.

The close agreement between the Mu^* hyperfine parameters for GaAs and GaP (see Table I) is remarkable considering how different $A_\parallel^*$ and $A_\perp^*$ are in the group IV crystals. The weak hyperfine interaction of Mu^* suggests that the unpaired electron spin density is concentrated on the neighboring atoms. Thus, the hyperfine parameters are expected to be particularly sensitive to the types of neighboring atoms and to their location. Indeed, a large variation in $A_\parallel^*$ and in $A_\perp^*$ is observed among Si, Ge, and diamond (see Table I). The near equality of the Mu^* hyperfine parameters between

TABLE I. Comparison of the hyperfine parameters and formation probabilities for Mu^* and Mu in semiconductors. (The formation probabilities F_{Mu} and F_{Mu^*} in the present work were determined by correcting the precession amplitudes for finite timing resolution (Ref. 15) and then normalizing to the free muon amplitude in Cu.) Only the relative sign between the Mu^* hyperfine parameters ($A_\parallel^*$ and $A_\perp^*$) is known experimentally. For comparison the hyperfine constant for muonium in vacuum (A_{Mu}/h) equals 4463.302 MHz.

	Temp. (K)	$A_\parallel^*/h$ (MHz)	$A_\perp^*/h$ (MHz)	F_{Mu^*} (%)	A_{Mu}/h (MHz)	F_{Mu} (%)
GaAs	10	217.8(2)	87.74(6)	35(5)	2883.6(3)	63(6)
GaP	10	219.0(2)	79.48(7)	18(3)	2914(5)[a]	72(10)[a]
Si		16.82(1)[b]	92.59(5)[b]	39(3)[c]	2006(2)[d]	56(5)[c]
Ge		27.27(1)[b]	131.04(3)[b]	25(10)[e]	2359.5(2)[d]	35(5)[e]
Diamond		−167.98(6)[b]	392.59(6)[b]	12(1)[f]	3711(21)[d]	20(4)[f]

[a]Reference 14.
[b]References 1, 2, and 17. Values are extrapolated to 0 K.
[c]Reference 18. Values are for p-type Si.
[d]Reference 15. Values are extrapolated to 0 K.
[e]Reference 16. $T = 10$ K.
[f]Reference 1. $T = 4.2$ K.

GaAs and GaP suggests that the local crystalline environment is similar. The location most compatible with this requirement is an As or a P vacancy, since in both GaAs and GaP the vacancy has four Ga nearest neighbors with 12 As or 12 P next-nearest neighbors 63% farther away.

Estle has suggested that Mu* is substitutional muonium in group IV crystals.[10] Sahoo, Mishra, and Das have proposed a three electron muon-vacancy center with a charge of +2 in group IV crystals,[8] which would have a charge of +1 for a group V vacancy in a III-V compound. Preliminary theoretical calculations on group IV crystals have been done by Sahoo *et al.*[8] and by Mainwood, Estle, and Stoneham[9] with encouraging results.

There are, however, some difficulties with the vacancy model. For instance, the process by which the muon ends up substitutional is not well understood. There is no significant missing muon polarization. This implies that Mu* must form within a few ns after implantation if the bare muon is the precursor to Mu*, or even faster if Mu is the precursor.[20] Since the concentration of single vacancies is too small to account for such rapid formation, the vacancy model requires that the muon creates its own vacancy and becomes trapped epithermally or immediately after thermalization. The feasability of such a mechanism has not been demonstrated. In addition, if Mu* were to form in this way, one might expect to observe other charge states of the muon-vacancy complex. Inspection of Table I reveals, however, that Mu and Mu* account for most of the measured muon polarization: Therefore, the probability of formation for other centers must be very small.

Let us now examine the isotropic hyperfine parameters of Mu in GaAs and GaP (see Table I). It is surprising to find them so similar also. In Si, Ge, and diamond Mu is localized at the tetrahedral interstitial site or moving rapidly between such sites. There are two inequivalent tetrahedral interstitial sites in GaAs and in GaP: one site has four Ga nearest neighbors and six As (or P) next-nearest neighbors approximately 15% farther away; the other tetrahedral site has four As (or P) nearest neighbors with six Ga next-nearest neighbors. The equivalent tetrahedral sites are separated by an inequivalent site and thus one expects a much larger barrier to Mu diffusion in compound materials compared with elemental materials. This is confirmed by measurements of the Mu line broadening in high resistivity GaAs at low applied magnetic fields, which indicate there is no significant averaging of the nuclear hyperfine interaction due to motion. Since we observe only one type of Mu center with nearly equal hyperfine parameters in GaAs and GaP, the observed center might correspond to the tetrahedral site with Ga nearest neighbors. The lack of any appreciable influence from the nearby As (or P) next-nearest neighbors is remarkable and will require a detailed theoretical analysis.

Additional measurements were also made on low-resistivity crystals of the group III-V semiconductors GaSb, InP, InAs, and InSb, and on a high-resistivity InP crystal (Fe doped). However, no paramagnetic centers were detected; instead, a large free muon signal was observed.

In conclusion, by extending the observation of muonium defect centers to GaP and GaAs we find centers whose properties are quite similar in many ways to those of the normal and anomalous muonium centers observed in diamond, Si, and Ge. Yet there are two major differences between the results in the III-V compounds and in the group IV crystals. Anomalous muonium in both GaAs and GaP has $|A_{\parallel}^*| > |A_{\perp}^*|$, just the opposite to what is found in the three elemental semiconductors. Furthermore, both the Mu and the Mu* hyperfine parameters are very close in GaAs and GaP, whereas they differ substantially in the group IV crystals. The reasons for this are not clear.

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