Pressure-Induced Shallow-to-Deep Donor-State Transition in ^{119}Sn-Doped GaAs Observed by Mössbauer Spectroscopy

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The Sn *DX* center in GaAs, a deep donor state of Sn, has been observed by Mössbauer measurements at high pressure. The size of the pressure-induced Sn *DX* Mössbauer resonance compared to the net conduction-electron concentration at zero pressure provides evidence that the Sn *DX* center localizes two or three electrons in the ground state.

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Substitutional donors in $Al_xGa_{1-x}As$ yield shallow hydrogenlike levels as well as deep metastable states for $x \geq 0.2$.[1] High pressures[2] above about 2.4 GPa or very heavy doping[3] both demonstrate the existence of these metastable states in *n*-type GaAs. Thus, band-structure changes that are induced by Al alloying *or* by hydrostatic pressure, as well as changes in the Fermi level, cause electrical activation of deep metastable states associated with the donor atoms. These deep levels—the so-called *DX* centers[4]—have been a subject of considerable interest and controversy during the last decade.[5] There are at least two important questions that have yet to be solved: (1) What is the extent and geometry of the local lattice relaxation at the substitutional donor site in the electron-localized ground state and (2) how many conduction-band electrons are localized at each *DX* site in the ground state?

Regarding question (1), for several years the only information available was from ballistic phonon measurements[6] which provided evidence for trigonal and orthorhombic symmetry at the Sn and Te sites (in the ionized, conductive state), respectively. Recently, x-ray-absorption spectroscopy measurements yielded no evidence of large, symmetry-breaking dilatational lattice distortions in either Se-doped $Al_{0.38}Ga_{0.62}As$ (Ref. 7) or Sn-doped $Al_{0.3}Ga_{0.7}As$.[8] On the other hand, recent Mössbauer spectroscopy analysis[9,10] of ^{119}Sn-doped $Al_xGa_{1-x}As$ for $0 \leq x \leq 1$ finds a broadened resonance for $x = 0.3$–0.43 that suggests a Sn *DX* center with noncubic symmetry. However, alternative interpretations based on either two different *DX* centers or a distribution of *DX* centers were also suggested[9] and these would not necessarily require a lattice distortion at the Sn site to explain the broad Mössbauer line.

Regarding question (2), the generally assumed notion that the *DX* center localizes a single electron to become a neutral entity in the ground state (i.e., $Sn^+ + e \rightarrow DX^0$) has been questioned by recent suggestions[11,12] of a two-electron, negatively charged ground state based on a negative-*U* electron-electron correlation. One important reason for postulating this model was the lack of an electron-paramagnetic-resonance signal which would be expected for a single-electron ground state. However, the variation of the electron mobility with pressure in highly doped GaAs has been used to support the neutral-charge-state model.[13] The interpretation of mobility data remains controversial.[14] More recently, low-temperature magnetic-susceptibility studies indicated that Si and Te *DX* centers are paramagnetic donors with one unpaired electron[15] whereas high-pressure studies of GaAs simultaneously doped with Ge and Si support the two-electron, negative-*U* model.[16]

There has been one proposal which is a vacancy-antisite complex that captures three electrons.[17] The quantitative fractions of Sn that generated three different Mössbauer resonance lines[9] have recently been interpreted to support this rather complex defect.[18] The Mössbauer resonance of the Sn *DX* center has a significant positive isomer shift relative to the shallow Sn_{Ga} donor consistent with substantial electron localization.[9,10] However, the size of this shift cannot be used to give the number of localized electrons without complex calculations requiring model potentials.[19]

This Letter describes a high-pressure Mössbauer study of ^{119}Sn-doped GaAs which conclusively identifies the Sn *DX* center in GaAs and provides strong evidence that it localizes more than a single electron. The specimen subjected to pressure here had been grown by metal-organic vapor-phase epitaxy (MOVPE) and carefully analyzed in a previous systematic investigation of Sn-doped GaAs (Refs. 20 and 21) and $Al_xGa_{1-x}As$,[9,10] where van der Pauw characterization yielded a net carrier concentration of $(6 \pm 1) \times 10^{18}$ cm^{-3} and quantitative Mössbauer analysis[20,21] gave a total Sn concentration of $(8 \pm 1) \times 10^{18}$ cm^{-3}. The Mössbauer study[21] also demonstrated that (73 ± 5)% of the resonance was due to the Sn_{Ga} shallow donor site, which is in good agreement with the above carrier density (i.e., $0.73 \times 8 \times 10^{18}$ cm$^{-3} = 5.8 \times 10^{18}$ cm^{-3}). The isomer shift of a shallow donor is unaffected by its ionization state due to the highly delocalized nature of the electron even in the neutral state. The balance of the Sn (27%) was attributed to nonelec-

trically active (neutral) defects that could be Sn_{Ga}-Sn_{As} pairs, larger clusters, or even microprecipitates of Sn_3As_2.[21] The possibility that this second site is due to population of the *DX* center due to heavy doping[3] has been considered and ruled out by the absence of any persistent photoconductivity in our sample at low temperature. This result is consistent with Ref. 3 which shows that even heavier doping would be required to produce a *DX* population as large as the second-site fraction observed in our sample.

The high-pressure experiments were performed using methods described in detail elsewhere.[22,23] The ^{119}Sn-GaAs absorber, in the form of small single-crystal flakes, was mounted between the 8-mm-diam faces of B_4C anvils which are designed to allow minimum separation of the 15-mCi $^{119}Sn^m$-$CaSnO_3$ source and the detector. Pressure calibration was via the pressure dependence of the superconducting transition temperature of Pb.[22,23] The sample was kept in the dark while the pressure was applied at room temperature; it was then cooled (in the dark) to about 80 K where most data were accumulated. Some data were also taken at 4.2 K and showed no detectable differences in comparison to those at 80 K.

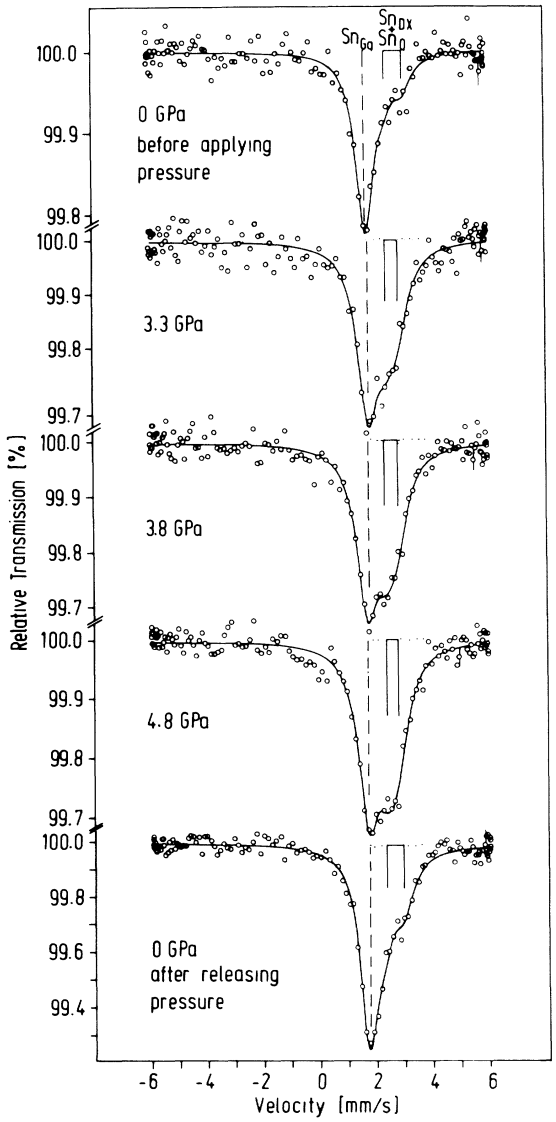

FIG. 1 Mössbauer spectra from ^{119}Sn-doped GaAs under pressure. The solid lines passing through the data are least-squares fits of a superposition of a single line (Sn_{Ga} site) and a doublet, fit type A. The enhanced resonance near 2.6 mm/s is attributed to pressure-induced electron localization to form Sn *DX* centers.

Figure 1 shows the 80-K Mössbauer spectra at (a) atmospheric pressure, (b) 3.3 GPa, (c) 3.8 GPa, (d) 4.8 GPa, and (e) after releasing the pressure. The obvious pressure-induced modification of the resonance is the enhancement of the resonance on the positive velocity side of the Sn_{Ga} zero-pressure resonance. To investigate carefully the nature of this new resonance two types of fitting procedures were used.

Fit A: singlet+doublet.—All spectra were fitted with a superposition of a singlet (Sn_{Ga}) and a doublet with all three lines restricted to have the same width and the doublet restricted to have both lines of equal intensity. This type of fit is shown in Fig. 1 and yields the solid curve passing through the data of each spectrum. The new resonance is accounted for by an increased fractional area of the doublet. Spectral parameters from the fits are given in Table I.

Fit B: two singlets+fixed doublet.—The three spectra at high pressure were also fitted with a superposition of singlet 1 (Sn_{Ga}), singlet 2, and a doublet, with the latter having a fixed fractional area of 30% (average of the two zero-pressure fit-A results) and a fixed quadrupole splitting (same as the zero-pressure value). All four lines were required to have the same linewidth. The new resonance is accounted for by singlet 2. Spectral parameters from this type of fit are included in Table I. The quality of the fits as indicated by values of χ^2 (listed in Table I) suggests that both fits A and B are equally satisfactory.

The isomer shift of the pressure-induced doublet (fit A) or singlet 2 (fit B) is 2.6 mm/s and is in good agreement with that identified as the Sn *DX* center in $Al_xGa_{1-x}As$ for $x=0.30$–0.43,[9,10] and therefore confirms this previous identification of the Sn *DX* center. It also provides strong evidence against the interpretation by Van Vechten[18] that the *DX* center has an isomer shift of 3.1 mm/s. Unfortunately, as a result of the fact that the new resonance can be fitted with either a doublet (fit A) or a singlet (fit B), the existence of a large lattice relaxation at the Sn *DX* site cannot yet be decided. In the event that the doublet fit is correct, then a quadrupole splitting of 0.4 mm/s corresponds to a field gradient of $V_{zz}\simeq 3.5\times 10^{15}$ esu/cm^3. Such a value is similar in magnitude to theoretical predictions of field gradients at impurities in GaAs associated with substantial lattice relaxation.[24]

We now interpret the quantitative fractions of the pressure-induced *DX* Mössbauer resonance. Assuming

TABLE I. Mössbauer spectral parameters of ^{119}Sn-doped GaAs at 80 K under pressure (P). δ is the isomer shift relative to $CaSnO_3$ at room temperature; Γ is the full linewidth at half maximum; Δ is the quadrupole splitting of the doublet. F is the fractional resonance area. Uncertainties in the last significant figures are given in parentheses. f in parentheses signifies that this parameter was fixed during the fitting.

P (GPa)	Fit Type	Spectral Component	δ (mm/s)	Γ (mm/s)	Δ (mm/s)	F (%)	χ^2
0[a]	A	singlet	1.77(3)	0.76(8)	0	75(6)	
		doublet	2.78(15)		0.65(f)	25(8)	
3.3(3)	A	singlet	1.78(5)	0.89(9)	0	55(5)	1.078
		doublet	2.63(7)		0.44(15)	45(9)	
	B	singlet 1	1.77(3)	0.85(8)		53(4)	1.073
		singlet 2	2.56(9)		0	17(3)	
		doublet	2.68(8)		0.65(f)	30(f)	
3.8(3)	A	singlet	1.75(4)	0.91(7)	0	52(5)	1.176
		doublet	2.60(5)		0.41(12)	48(7)	
	B	singlet 1	1.74(3)	0.88(6)	0	49(3)	1.185
		singlet 2	2.56(6)		0	21(3)	
		doublet	2.60(8)		0.65(f)	30(f)	
4.8(3)	A	singlet	1.74(3)	0.92(f)	0	50(3)	1.158
		doublet	2.60(4)		0.37(9)	50(3)	
	B	singlet 1	1.73(2)	0.92(5)	0	48(2)	1.178
		singlet 2	2.60(4)		0	22(2)	
		doublet	2.60(f)		0.65(f)	30(f)	
0[b]	A	singlet	1.77(2)	0.83(4)	0	66(3)	
		doublet	2.65(6)		0.65(f)	34(4)	

[a]Before pressure applied. [b]After pressure applied.

transfer of electrons from the Γ continuum to the DX states under pressure, and extrapolating available data[25] on the pressure dependence of Sn DX centers, the Γ band should be completely empty at about 3–4 GPa. The position of Sn DX states in GaAs under hydrostatic pressures has been deduced from Shubnikov-de Haas measurements[25,26] for Sn-doped samples grown via molecular-beam epitaxy (MBE) with zero-pressure carrier concentrations close to that of the sample studied here. We have also made magnetotransport measurements (Hall and Shubnikov-de Haas) on a Sn-doped sample (5×10^{18} cm^{-3}) grown by MOVPE under conditions very similar to those used to produce our Mössbauer sample. A maximum of 1.5 GPa was reached and the behavior was identical to that observed from the MBE samples,[25,26] i.e., a dramatic reduction of the carrier concentration above 0.5 GPa. If each Sn DX center localized a single electron then the singlet resonance due to Sn_{Ga} should *disappear* at 3–4 GPa and this obviously does not occur (Fig. 1, Table I). The previous Mössbauer study[9] of Sn DX centers in $Al_xGa_{1-x}As$ also found that the resonance attributed to the Sn_{Ga} site remained at a fraction of about 40% in the range of x where maximum DX-center formation is known to occur.

Two conceivable causes for the apparent retention of the Sn_{Ga} resonance at high pressure in GaAs and in $Ga_{1-x}Al_xAs$ with $x=0.3$–0.4 are (i) Sn-related acceptors are present with a Mössbauer resonance indistinguishable from that of the Sn_{Ga} shallow donor or (ii) more than one electron is required to stabilize each Sn DX center (e.g., $Sn_{Ga}^{+}+2e\rightarrow DX^{-}$ or $Sn_{Ga}^{+}+3e\rightarrow DX^{--}$), thereby converting only a *fraction* of the available Sn_{Ga} sites into DX centers (e.g., 50% or 33% for the above examples, respectively).

First, consider (i), the issue of partial compensation. As noted above, the Hall carrier concentration agreed well with the concentration of Sn_{Ga} determined quantitatively from the Mössbauer resonance intensity, suggesting that the sample is uncompensated (i.e., $N_A \ll N_D$, where N_D and N_A are shallow donor and acceptor concentrations, respectively). However, we cannot rule out partial compensation for the following reasons. Our previous Mössbauer and Hall studies[20,21] of Sn-doped GaAs demonstrated that highly compensated samples (produced by annealing under As-rich atmosphere) have Sn-related acceptors with a Mössbauer resonance that could not be distinguished from the Sn_{Ga} shallow donor resonance. Thus, our value of 6×10^{18} cm^{-3} for the Sn_{Ga} site concentration should be regarded as the value of N_A+N_D. The Hall measurement of N_D-N_A assumed a Hall coefficient of unity which may not be valid at such high carrier concentration. To examine more carefully the possibility of partial compensation in our high-pressure sample, we prepared two additional samples by MOVPE with similar Sn concentrations and characterized them with both Hall (van der Pauw) and Shubnikov-de Haas (SdH) measurements. For both samples the net carrier concentrations determined by SdH were about 70% of those determined by the Hall method. Taking the SdH value as more reliable, then a corrected value of 70% of the Hall value for our high-pressure sample would be $N_D-N_A=4\times10^{18}$ cm^{-3}. This analysis suggests that a partial compensation ratio of $N_A/N_D=1/6$ may be appropriate (at zero pressure).

Now, consider (ii), the issue of the number n of conduction electrons required to stabilize each DX center. The concentration of DX centers at the maximum pressure can be obtained from the experiment. The zero-pressure doublet is due to an electrically inactive Sn, as interpreted elsewhere,[21] and we assume that it is unaffected by pressure. The DX fraction is then given by F(doublet) -30% for fit A and is given by F(singlet 2)

for fit B. Both of these fits yield a maximum DX fraction under pressure of about 20% (Table I) at 4.8 GPa. This yields a DX concentration of $N_{DX}=1.6\times10^{18}$ cm^{-3} (20% of 8×10^{18} cm^{-3}, the total Sn), and therefore $n=(N_D-N_A)/N_{DX}=4/1.6=2.5$ electrons. A conservative estimate of uncertainty in this value is $\simeq\pm0.7$ electron based on the statistical uncertainty from the computer analysis of the DX resonance fraction ($\simeq$20%) and the uncertainty in conduction-electron concentration ($\simeq$20%). There is an additional uncertainty due to the fact that the Mössbauer recoilless fraction f can be site dependent. For example, if the Sn DX site has a recoilless fraction at 80 K that is 20% smaller than that for the Sn_{Ga} site at 80 K (due to weaker bonding in the lattice), then the value of n should be recomputed as $4/(1.6\times1.2)=2.1$ electrons. Since a 20% difference at liquid-nitrogen temperature represents a conservative estimate of the maximum variation in f for Sn in a variety of sites in GaAs and in other compounds,[27] we include a possible error of 20% in n. Our final result is $n=2.5\pm0.9$ electrons, i.e., each Sn DX center is a multiple-electron trap that localizes two or three electrons in its ground state. A similar analysis[18] of ^{119}Sn-$Al_xGa_{1-x}As$ results[9] is less reliable due to unknown variations in compensation and dopant clustering versus x, but it yielded $n=2$–3, consistent with the present results.

The only way to reconcile our Mössbauer and Hall data and the possibility of a single electron localized at the Sn DX center is the existence of an unusual (high-pressure) phenomenon that prevents complete loss of electrons from the Γ continuum. For example, the simple extrapolation of energy levels based on experimental transport data[25,26] may not be valid. If the energy level is sufficiently shallow, it may not be fully occupied at 80 K. However, *no further increase* in the DX resonance fraction was observed upon cooling to 4.2 K. Another possibility is that the procedure of applying the pressure at room temperature and then cooling may prevent the thermal equilibration of the DX states. However, neither photoconductivity studies nor Shubnikov-de Haas experiments of similar Sn-doped samples have shown evidence of significant departures from equilibrium.[28]

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