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^{119}Sn Mössbauer study of shallow and deep states of Sn in $Ga_{1-x}Al_xAs$

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Epitaxial layers of $Ga_{1-x}Al_xAs$ ($0 \le x \le 1$) doped with ^{119}Sn-enriched tin have been grown by metal-organic vapor-phase epitaxy and characterized by ^{119}Sn Mössbauer spectroscopy and Hall measurements. The $x=0$ and $x=1$ samples yield Mössbauer spectra that are interpreted in terms of two Sn sites corresponding to substitutional shallow donors and clustered species, with the former site population clearly dominating. The $x=0.3$–0.4 samples yield significantly altered Mössbauer resonance with a new type of dominating site. This can be interpreted as due to the *DX*-center deep level with an electronic structure altered due to electron localization and a local distortion of cubic symmetry in accord with recent models.

INTRODUCTION

The ternary semiconductor alloy system $Ga_{1-x}Al_xAs$ has been and is being extensively studied because of its importance and further promise in high-speed and optoelectronic devices. Its value stems primarily from the ability to adjust the band gap (via suitable x) without changing the lattice constant, a crucial consideration in epitaxial growth. However, a severe problem arises in association with n-type doping of $Ga_{1-x}Al_xAs$. Independent of the nature of the dopant and the epitaxial-growth method, donor incorporation leads to similar features:[1] for $x<0.2$ the dopant introduces a shallow level a few meV from the conduction band; for $x>0.2$, in addition to the shallow donor, a deep donor appears with a thermal activation of the order of 10^2 meV; furthermore, in this compositional range persistent photoconductivity (PPC) is observed. The deep level, the so-called "*DX* center,"[1] is a substitutional donor that is most often associated with the L-band minimum.[2-10] Several recent studies have shown that in the region of interest, $0.2<x<0.7$, shallow and deep donors exist simultaneously.[8-12]

In a previous paper,[13] further details were reviewed and information on donors in Sn-doped $Ga_{1-x}Al_xAs$ was derived from Hall and photoluminescence measurements. The present investigation uses Mössbauer spectroscopy to obtain information on Sn incorporation in $Ga_{1-x}Al_xAs$ and to search for the atomic-scale nature of the deep donor. At this point, it is appropriate to review pertinent models proposed to explain the *DX* center in order to suggest expected alterations in the Mössbauer resonance of a dopant that converts to such a center from a shallow-donor type of site.

Deep levels in semiconductors are usually described on the basis of the linear combination of atomic orbitals (LCAO) theory. However, in $Ga_{1-x}Al_xAs$ the fact that the deep level is independent of n-type doping species leads one to seek a more appropriate model. A multivalley, effective-mass model that includes intervalley contributions can give a good fit to experimental data.[7,8,11,14] Unfortunately, such models do not explain PPC.

At an early stage in the investigation of *DX* centers, Lang *et al.* proposed[15] and expanded upon[3] a large-lattice-relaxation model to explain PPC.[16] They introduced a configuration-coordinate model for the *DX* center and argued that its microscopic origin could be a complex involving a donor and an arsenic vacancy, V_{As}. Subsequently, evidence for a reduction in local symmetry at the *DX* center was provided by measurements of the attenuation of ballistic phonons.[17] Trigonal and orthorhombic symmetries for Sn and Te, respectively, were reported in support of a Sn-vacancy nearest-neighbor complex (Sn_{Ga}-V_{As}) and a Te-vacancy next-nearest-neighbor complex (Te_{As}-V_{As}).[17] However, the existence of sufficient concentrations of V_{As} in $Ga_{1-x}Al_xAs$ grown by metal-organic vapor-phase expitaxy (MOVPE) or molecular-beam epitaxy (MBE), which both operate with a large excess of As vapor, is rather unlikely. The Mössbauer resonance of such a complex, Sn_{Ga}-V_{As}, should be significantly different from Sn_{Ga}, the shallow donor. Ion-implantation studies[18] provide evidence for such a Sn site and its isomer shift corresponds to a dehybridization from the sp^3-like configuration toward an s^2p^2-like structure. A quadrupole splitting was also observed, as would be expected due to the lowering of the local symmetry by the V_{As} neighbor. However, this site was found to be unstable upon annealing above 200 °C,[18] a temperature much lower than used in LPE (liquid-phase epitaxy), MOVPE, or MBE growth.

Since *DX* centers are defects that are suggested to be strongly coupled to the lattice, a model based on local effects due to Al alloying has been introduced by

Kobayashi *et al.*[19] The stability of the sp^3 bonding between donor and host surrounding atoms is considered in the indirect-band-gap alloy regime. They assume that an instability in the sp^3 bond occurs due to the anisotropic distribution of Al and Ga atoms as nearest neighbors to the As site or next-nearest neighbors to the Ga site. The suggested result is a bond reconstruction of the donor atom on the As site into an sp^2- or even sp-like configuration. Specific modeling was done for Te and Si doping.[19]

The *DX* center was shown to appear in GaAs under hydrostatic pressure above 3 GPa based on photoluminescence,[20,21] deep-level transient-spectroscopy (DLTS),[22,23] photoconductivity,[24,25] and Shubnikov–de Haas[25] studies. Such results demonstrate that the emergence of the *DX* center is related to a change in band structure from GaAs- to (GaAl)As-like, comparable to what happens in $Ga_{1-x}Al_xAs$ as x increases. In other words, the deep donor in $Ga_{1-x}Al_xAs$ does not depend on the formation of any chemical complex involving Al atoms or vacancies. One of these high-pressure investigations[23] provides evidence of large lattice relaxation.

Oshiyama and Ohnishi[26] recently proposed a model in which the donor Si atoms on the Ga site are surrounded by a distorted As tetrahedron. The model is supported by calculations of the energy-level structure of clusters. The antibonding state of the donor shifts downward in the band gap upon distortion of the As surroundings. It was suggested that this model could be extended to GaAs under pressure since the local presence of Al is not required to generate the deep level.[26]

Morgan[27] pointed out that electrons bound to the donors can occupy either shallow or deep states. Transition between the two states involves a large lattice relaxation. The *DX*-center deep state is derived from a triplet of symmetry T_2, the donor being displaced from its centered lattice position. This displacement resembles a Jahn-Teller effect, the origin of which was suggested as follows:[27] the T_2 state is formed from the four nearest-neighbor antibonding orbitals; the component of this state having a symmetry axis along one of the $\langle 111 \rangle$ axes has $\frac{3}{4}$ of the electron probability density in this orbital and only $\frac{1}{4}$ in the other three; displacing the central atom along $\langle 111 \rangle$ away from the nearest neighbor in this direction lowers the total energy of the state. Many of the experimental observations on *DX* centers are qualitatively explained by this model.[27] Hasegawa and Ohno[28] have also suggested that *DX* centers are antibonding states arising from the donor impurities and that the shallow–deep-donor transition may require some lattice distortion to stabilize the antibonding state.

In contrast to the models just discussed, which imply large lattice relaxation, other authors[29–31] have discussed the existence of *DX* centers in a band-structure model[14] which involve little or no lattice distortion. In the band model, deep levels with small lattice relaxation can also explain most of the properties of *DX* centers, including PPC on the basis of a forbidden transition.[14,29–31] A recent structural calculation, based on a tight-binding method, supports a small lattice relaxation[32] and more recently an extended x-ray-absorption fine-structure experiment found no evidence for large lattice relaxation at the Se *DX* center.[33]

Two Mössbauer isotopes that can be used to study the deep level in $Ga_{1-x}Al_xAs$ are ^{119}Sn and ^{125}Te. ^{119}Sn was chosen for this initial study because of its narrower resonance linewidth relative to the size of the hyperfine interactions (isomer shift and quadrupole splitting) typically observed. Both isotopes have been used previously to study Sn (Ref. 34) and Te (Refs. 35 and 36) incorporation in LPE-grown GaAs, and in a recent paper[37] Sn doping of MOVPE-grown GaAs is investigated and provides the primary basis for interpretation of the present results. In general, one can suggest that a highly localized electron on the neutral *DX* center ($T < 100$ K) should produce a change in the electron density at the nucleus and therefore an isomer shift relative to that of the shallow donor state. The latter is well established for Sn in GaAs.[37] The size of such a shift will depend on the relative amounts of *s*- and *p*-like character and the degree of localization of the trapped electron. 5*p* electrons tend to shield the 5*s* electrons and reduce the contact electron density.[38] Superimposed on this effect will be the possible alteration in the original sp^3-like electronic structure due to a large lattice relaxation. The latter will also lead to a local electric field gradient at the donor nuclear site and therefore a quadrupole interaction would produce a splitting of the ^{119}Sn transition into a doublet. The size of the splitting will depend directly on the degree of the distortion and this will be a crucial factor in distinguishing between the large- and small-lattice-relaxation models.

EXPERIMENT

Sample preparation

Thick layers of $Ga_{1-x}Al_xAs$ with doping densities of 10^{18}–10^{19} cm^{-3} are needed to obtain satisfactory Mössbauer transmission spectra.[34–37] Nonequilibrium growth methods such as MBE or MOVPE are required in order to provide epilayers of constant x throughout the thick layers. Tin doping via MBE results in a Sn-rich accumulation layer at the surface.[39] MOVPE was used to grow the samples for this study. Preparation details are given in Ref. 37. Table I lists the deposition temperature, T_D, the ratio P_{Sn}/P_{Ga+Al} in the vapor phase, and the composition value x for each sample. The value of x was obtained by electron-microprobe analysis. The readily oxidizable compound AlAs was coated with a 50-nm layer of GaAs as the final step in the growth process. This prevented electrical characterization.

Electrical measurements

$Ga_{1-x}Al_xAs$ samples were grown on semi-insulating {100} GaAs substrates and, before preparation for transmission Mössbauer measurements, the electrical properties were measured by the van der Pauw method at 77 and 300 K. To limit the incorporation of neutral species,[37] the ratio P_{Sn}/P_{Ga+Al} in the vapor phase was restricted to values lower than 0.006, except for the $x=1$

sample. As previously discussed for $Ga_{1-x}Al_xAs$, Hall measurements do not give a straightforward evaluation of the shallow- and deep-donor densities.[13] Around the crossover composition, the Γ, L, and X valleys lie close together; therefore n_H is not related in a simple way to the carrier density. Experimentally, for a constant concentration of n-type dopant a large decrease in n_H is observed near the crossover, as shown in Fig. 1.

The degree of compensation in $Ga_{1-x}Al_xAs$ MOVPE-grown epilayers is usually high. C is the most likely acceptor and has been measured at a concentration of $\sim 10^{17}$ cm^{-3}.[40] In addition, acceptor species like Sn_{Ga}-V_{Ga} might be incorporated.[34,37,41] (GaAl)As is usually grown under high P_{As}/P_{Ga+Al} ratio (50–100). This could produce a higher V_{Ga} concentration at the growing interface than in the growth of GaAs, which utilizes a lower P_{As}/P_{Ga} ratio (20–40). Nonactive species are very likely to be incorporated at the high doping levels used here.[34,37] Note from Table I that two samples, $x=0.30$ and 0.43, were grown with lower P_{Sn}/P_{Al+Ga} ratios. The mobilities of these samples are significantly better than other samples, thus supporting lower compensation and lower incorporation of nonactive species.

Mössbauer measurements

The ^{119}Sn Mössbauer measurements were carried out as described in Ref. 37. Figure 2 shows 76-K Mössbauer spectra from samples with Al composition from GaAs to AlAs. Each spectrum required from 100 to 300 h of accumulation time to acquire about $(1-2)\times 10^7$ counts per channel over the 256 channels. To obtain satisfactory least-squares fits with the χ^2 indicator near unity, it was necessary to include three Lorentzian lines and these are labeled as 1, 2, and 3 in Fig. 2. The major qualitative variation with x is the enhanced resonance from lines 2 and 3 for $x=0.30$, 0.40, and 0.43. The fits shown were made with the single restriction that the three lines have the same linewidth. The spectral parameters obtained from these fits are listed in Table II. Also included in Table II are values of the total Sn concentration based on the resonance area and sample thickness as described in Ref. 34. The recoilless fraction associated with all three lines was taken as 0.67 at 76 K, corresponding to an effective Debye temperature of 200 K.[37]

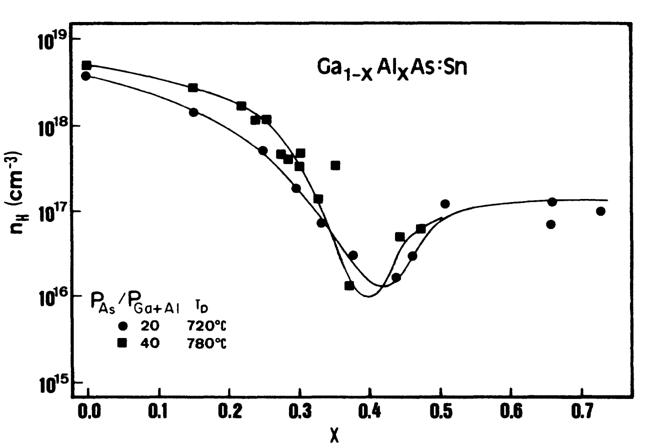

FIG. 1. Carrier concentration from Hall measurements from two series of Sn-doped samples (natural Sn rather than ^{119}Sn).

DISCUSSION

Sn in GaAs and AlAs

Resonance line 1 from the $x=0$ sample (GaAs, sample 2 in Ref. 37) has previously been identified as originating from the substitutional shallow donor Sn site, Sn_{Ga}, on the basis of a correlation of the Sn-site population associ-

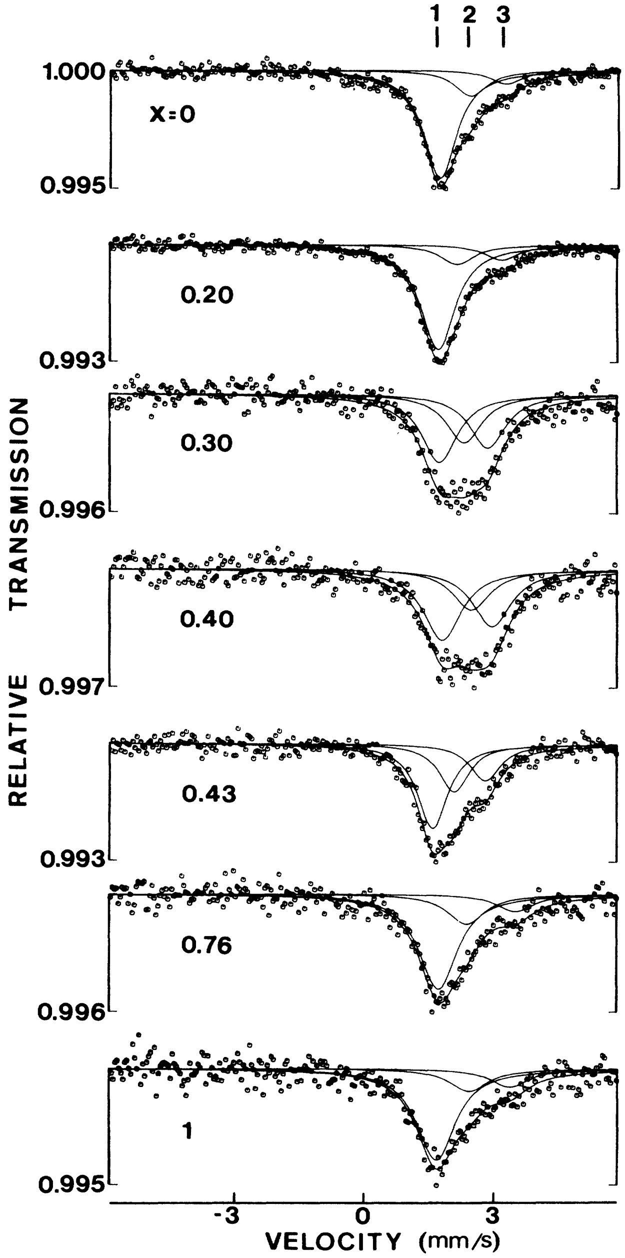

FIG. 2. Mössbauer spectra from ^{119}Sn-doped $Ga_{1-x}Al_xAs$. The solid line passing through the data is a least-squares fit of the three Lorentzian-shaped lines indicated.

TABLE I. Growth conditions and electrical characteristics of MOVPE-grown ^{119}Sn-doped $Ga_{1-x}Al_xAs$. P_{Sn}/P_{Ga+Al} represents the ratio of partial pressures of $Sn(CH_3)_4$ to $Al(CH_3)_3 + Ga(CH_3)_3$. T_D is the substrate temperature during deposition. n_H is the carrier concentration as determined by the Hall effect (van der Pauw geometry). μ is the Hall mobility. The Al fraction x was determined by electron-microprobe analysis.

x	P_{Sn}/P_{Ga+Al}	T_D (°C)	n_H (10^{18} cm^{-3}) 300 K	n_H (10^{18} cm^{-3}) 77 K	μ (cm^2/V s) 300 K	μ (cm^2/V s) 77 K
0	0.005	720	5.7	5.9	900	950
0.20	0.006	720	1.5	1.2	255	230
0.30	0.003	725	0.055	0.0085	1050	525
0.40	0.006	720	0.085	0.0054	175	110
0.43	0.0035	720	0.02	0.006	534	955
0.70	0.006	750	a		a	
0.76	0.004	750	0.29	-0.028[b]	210	270
1	0.015	720	c		c	

[a] Not measurable due to surface degradation.

[b] p type.

[c] Not measurable due to protective covering layer of GaAs.

TABLE II. Mössbauer spectral parameters of ^{119}Sn-doped $Ga_{1-x}Al_xAs$ at 76 K. Lines 1, 2, and 3 are indicated in Fig. 2. δ is the isomer shift relative to $CaSnO_3$ at room temperature. Γ is the full linewidth at half maximum resonance and was restricted to be the same for all three lines. F is the fractional resonance intensity. n_T is the total Sn concentration from all three sites. Statistical uncertainty (one standard deviation) in the last significant figures is given in parentheses.

Sample (x)	Line	δ (mm/s)	Γ (mm/s)	F (%)	n_T (10^{18} cm^{-3})
0	1	1.78(1)	0.91(3)	73(3)	8(1)
	2	2.50(6)		17(3)	
	3	3.30(7)		10(3)	
0.20	1	1.78(2)	0.97(3)	75(4)	8(1)
	2	2.22(10)		14(3)	
	3	3.26(5)		11(3)	
0.30	1	1.81(6)	1.01(8)	40(7)	5(1)
	2	2.39(13)		28(7)	
	3	2.94(7)		32(7)	
0.40	1	1.89(6)	1.08(9)	42(5)	8(2)
	2	2.57(20)		24(11)	
	3	3.05(10)		34(11)	
0.43	1	1.74(3)	0.89(5)	50(4)	6(1)
	2	2.26(5)		28(4)	
	3	3.02(4)		22(3)	
0.70	1	1.76(5)	0.93(9)	65(6)	5(2)
	2	2.38(24)		14(8)	
	3	3.02(10)		21(5)	
0.76	1	1.81(4)	1.08(7)	67(5)	4(1)
	2	2.47(11)		21(6)	
	3	3.57(10)		12(3)	
1	1	1.75(4)	1.09(9)	69(5)	9(2)
	2	2.53(19)		17(6)	
	3	3.48(14)		14(3)	

ated with line 1 and the free-carrier concentration.[34,37] Lines 2 and 3 from GaAs were previously fitted with a quadrupole doublet (subspectrum *B* in Ref. 37) and shown to be associated with electrically neutral Sn species that were suggested to be $Sn_{Ga}Sn_{As}$ pairs or microprecipitates of Sn_3As_2.[37] Our removal of the restriction of equal line intensities for lines 2 and 3 does not change the Mössbauer spectral parameters significantly for this $x=0$ sample (compare $x=0$ data in Table II with sample-2 data in Ref. 37).

The Mössbauer resonance from Sn in AlAs ($x=1$), reported here for the first time to our knowledge, is very similar to that of Sn in GaAs and strongly suggests the following interpretation: line 1 is from the Sn_{Al} shallow donor site and lines 2 and 3 are from clustered Sn species that are not electrically active. It was not possible to obtain Hall data to support this interpretation due to the protective layer of GaAs deposited over the AlAs to prevent oxidative decomposition. However, there are other reasons that support the assignment of line 1 as due to Sn_{Al}: (i) The lattice constant of AlAs is only about 0.001 nm larger than GaAs and the identical nearest-neighbor environment of four As atoms would suggest a very similar isomer shift for Sn_{Ga} and Sn_{Al}, as observed (Table II); (ii) systematic ion-implanation studies of Sn in III-V semiconductors by Weyer and co-workers[42] suggest that little or no change in isomer shift is expected for Sn_{Ga} in GaAs and Sn_{Al} in AlAs (e.g., the isomer shifts of Sn_{Ga} in GaAs and Sn_{In} in InAs are identical within experimental error[42]); (iii) spatial charge-density calculations for GaAs and AlAs demonstrate very similar distributions.[43,44] There is one significant difference in the spectral parameters from the $x=0$ and 1 samples: the linewidth from the $x=1$ sample is about 20% larger. This may be indicating additional weak hyperfine interactions associated with other sites such as the shallow acceptor, Sn_{As}. The ion-implantation results show systematic isomer shifts of about $+0.1$ mm/s for Sn in the group-V site compared to the group-III site.[42] Also, vacancy-associated Sn sites such as Sn_{Al}-V_{Al} may produce only line broadening due to their expected similar isomer shift and weak quadrupole interaction as discussed for Sn_{Ga}-V_{Ga} sites in GaAs.[34,37] The detection of *p*-type conductivity in the $x=0.76$ sample (Table I) and the low values of n_H in Fig. 1 near $x=0.7$ provide evidence for strong compensation in the high-*x* regime.

Sn in $Ga_{1-x}Al_xAs$

Figure 3 shows the variation of the fractional resonance intensity of lines 2 and 3 versus *x*. Note that this fraction peaks near $x=0.3$–0.4 and mimics the peaks in the concentration of *DX* centers or their activation energy observed in $Ga_{1-x}Al_xAs$,[2,3,7,8,19,45,46] and it coincides with the minimum in n_H shown in Fig. 1 and seen by others.[45,47] A maximum in the persistent photoconductivity effect is also seen near $x=0.3$.[8] We therefore associate the resonance from lines 2 and 3 above the shaded area in Fig. 3 with the Sn *DX* center.

Before considering this hypothesis further, we must consider two alternate possibilities: (1) since lines 2 and 3 for $x=0$ are known to be due to neutral clusters or precipitates of Sn,[34,37] then the increased signal from lines 2 and 3 (at the expense of line 1) could be due to enhanced clustering of Sn during deposition in the crossover region of *x*, or (2) the modified resonance could be associated with alloy compositional disorder. Possibility (1) does not seem likely because (i) the sample with $x=0.30$ was prepared with a P_{Sn}/P_{Ga+Al} ratio reduced by a factor of 2 compared to the $x=0.20$ and 0.40 samples, (ii) the isomer shift of line 3 shows a systematic decrease (Table II) for the samples with large fractions of lines 2 and 3, suggesting that the nature of the Sn sites in these samples is different from that of the other samples (low or high *x*), and (iii) such a strong dependence of Sn solubility on band structure is unlikely.

Possibility (2) can be ruled out since alloy disorder can be expected to produce only a slight line broadening of line 1 and this should be approximately symmetric about the position of line 1, rather than heavily weighted toward higher velocity where lines 2 and 3 are located. This is due to the fact that the alloy disorder affects the second-nearest neighbors of the Sn_{Ga} or Sn_{Al} (Sn_{III}) sites and the Mössbauer effect is much less sensitive to second-neighbor alterations compared to those in the first-neighbor shell. For example, disordered $ZnSnP_2$ and $ZnSnAs_2$, in which only the second neighbors of the Sn are disordered, yield Mössbauer spectra that are broadened by about 25–30% compared to the ordered phase and the isomer shift produced upon disordering is less than 0.04 mm/s.[48] In addition, alloy disorder should produce the largest effect at $x=0.5$ and show a smoother variation with *x* than that displayed in Fig. 3.

Associating the enhanced resonance of lines 2 and 3

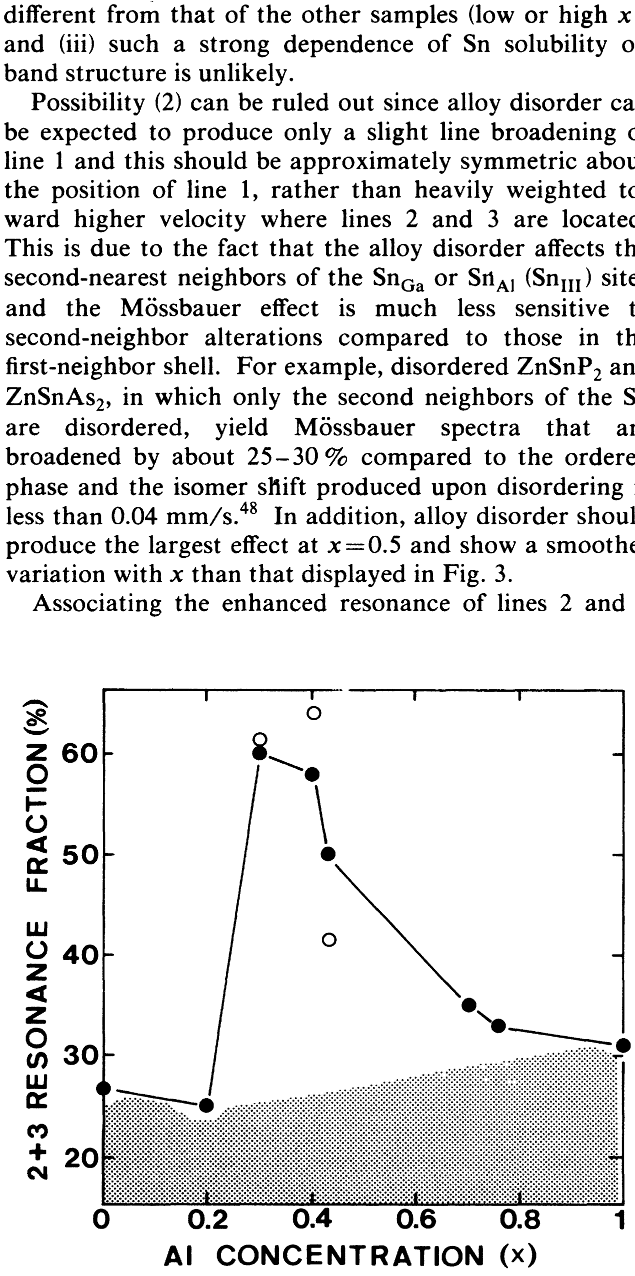

FIG. 3. Summed Mössbauer resonance fraction of lines 2 and 3 vs Al concentration. Solid circles from Table II. Open circles from Table III. Line is drawn to guide the eye. Region above shaded area is attributed to *DX* centers (see text).

with the Sn *DX* centers, we now consider the implications. There are at least three interpretations: (1) the two lines represent a quadrupole pair due to a single type of *DX* center, (2) the two lines represent two distinct types of deep donor defects, and (3) the two-line fit is accounting for a distribution of *DX* centers.

Single DX center

A single type *DX* center with a unique electric field gradient (EFG) at the Sn nucleus and no preferred orientation of the principal axes of the EFG relative to the γ-ray beam would yield a single quadrupole doublet with an intensity ratio of unity for the two lines. The three samples with large fractions of lines 2 and 3, $x=0.30$, 0.40, and 0.43, have line 2 to line 3 intensity ratios that are different from unity, but the statistical uncertainty does not rule out such a ratio (Table II). The Mössbauer spectra from these three samples were refitted with the following restrictions: line 1 (shallow donor) is restricted to be at 1.80 mm/s, lines 2 and 3 have equal intensities, and all three lines have the same linewidth. The results are listed in Table III. The χ^2 indicator was only slightly larger in all three cases than those obtained from the fits shown in Fig. 2 and Table II. The fractions of quadrupole doublet are shown in Fig. 3 for comparison (open circles). The isomer shifts and quadrupole splittings (Δ) are the same within the statistical uncertainty for all three samples. Averaging the values yields $\delta=2.67(5)$ mm/s and $\Delta=0.6(1)$ mm/s. Since the electrically inactive (clustered) species have similar parameters, their presence at the 25–30 % level, indicated by the shading in Fig. 3, is not strongly influencing these proposed *DX*-center parameters.

In order to estimate the change in electronic structure of the neutral Sn *DX* center compared to the $\mathrm{Sn_{III}}$ shallow donor, we use the semiempirical relation between isomer shift and effective numbers of 5*s* (n_s) and 5*p* (n_p) electrons developed by Lees and Flinn:[38,49]

$$\delta = A + 3.01 n_s - 0.20 n_s^2 - 0.17 n_s n_p ,$$

where *A* is a constant depending on the reference material and the absorber temperature. For a $\mathrm{CaSnO_3}$ (or $\mathrm{BaSnO_3}$) reference at room temperature and the sample at 77 K, $A=-0.38$ mm/s.[38] From the value of $\delta(\mathrm{Sn_{III}}$, shallow ionized donor$)=1.80$ mm/s,[37] and assuming that $n_p=3$, the above expression yields $n_s=0.94$. Taking δ(neutral Sn *DX* center$)=2.67$ mm/s and again assuming $n_p=3$, we obtain $n_s=1.38$; i.e., this would suggest that an additional 0.4 of a 5*s* electron is localized at the Sn *DX* center in the neutral state at 77 K compared to the shallow Sn donor at 77 K. We recognize that this is a crude estimation of the change in electronic structure and that recent studies[50] suggest quite different occupation numbers from those estimated above for the $\mathrm{Sn_{Ga}}$ site. For example, the diamond Sn phase, α-Sn, is calculated[50] to have an electronic structure represented by $5s^{1.41}5p^{1.77}5d^{0.13}$. A further discussion of these points is presented elsewhere.[51]

TABLE III. Mössbauer spectral parameters from quadrupole pair fits to lines 2 and 3. Line 1 (Fig. 2) was fixed at 1.80 mm/s and all lines were restricted to have the same linewidth. Δ is the quadrupole splitting and other symbols are the same as in Table II. Statistical uncertainty (one standard deviation) in the last significant figure is given in parentheses.

Sample (x)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	F (%)
0.30	2.63(6)	0.56(9)	1.00(6)	61(5)
0.40	2.74(6)	0.60(9)	1.01(6)	64(5)
0.43	2.63(8)	0.69(11)	0.95(4)	42(4)

The quadrupole splitting of $\Delta=0.6$ mm/s would suggest a substantial deviation from cubic T_d symmetry at the Sn *DX* center. This is based on a simple comparison with the quadrupole splitting at Sn sites in β-Sn (0.3 mm/s) (Refs. 34 and 52) and $\mathrm{Sn_3As_2}$ (0.5 mm/s) (Ref. 34), which are both significantly distorted from cubic symmetry, but have electronic structure similar to that of the Sn *DX* center, as indicated by their isomer shifts [$\delta(\beta\text{-Sn})=2.62$ mm/s (Ref. 34) and $\delta(\mathrm{Sn_3As_2})=2.79$ mm/s (Ref. 34)]. There is no simple relation between Δ and the degree of distortion because of the complex interplay between valence-electron and lattice contributions to the EFG.[53] Model calculations based on the distortions proposed by Morgan[27] and by Oshiyama and Ohnishi[26] are underway.

Two DX centers

The two resonance lines 2 and 3 may be interpreted in terms of two distinct types of *DX* centers, each with little or no quadrupole splitting (the slightly broadened linewidths of 1.01 and 1.08 mm/s observed for $x=0.30$ and 0.40 compared to 0.91 mm/s for $x=0$ could be caused by alloy disorder). There are at least two reports of evidence for two types of Sn-related deep levels in $\mathrm{Ga_{1-x}Al_xAs}$ that are characterized by a significant difference in location within the energy gap.[46,54,55] The deeper state would have a higher degree of electron localization in the neutral state and therefore a larger isomer shift. Computing average values of the isomer shifts from Table II, $\delta(2)=2.4(2)$ and $\delta(3)=3.00(5)$, and using the semiempirical relationship given above, we estimate $n_s(2)=1.2$ and $n_s(3)=1.54$. This interpretation therefore would suggest electron localization of about 0.3 and 0.6 of a 5*s* electron on the different Sn *DX* centers compared to the $\mathrm{Sn_{III}}$ shallow donor at liquid-nitrogen temperature.

Distribution of DX centers

A third interpretation of the Mössbauer result is suggested on the basis of recent experiments of Mooney *et al.*[56,57] which provide strong evidence that the *DX* center is not a single type of center, but probably is a group of similar centers exhibiting a distribution of capture cross sections and ionization depths. This distribution is suggested to result from the random distribution of group-III atoms in the alloys. This would lead to a distribution of electron localization and hence to a distribution of isomer shifts. The incomplete resolution of lines 2 and 3 permits this resonance to be interpreted also as a single broad resonance due to such a distribution. In this case the average isomer shift of $\delta=2.7$ mm/s and the splitting $\Delta=0.6$ mm/s from the quadrupole-pair fits would be measures of the average degree of localization and the width of the distribution, respectively. If a single large lattice relaxation, as suggested,[56-58] is superimposed on this distribution, then the experimental Δ is due in part to the deviation from cubic symmetry and in part to the distribution in isomer shifts.

SUMMARY

^{119}Sn Mössbauer spectroscopy provides clear evidence for *DX* centers in Sn-doped $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ that have significantly modified electronic structure in the neutral state compared to the shallow Sn donors. The population of these centers is maximum for $x=0.3-0.4$, in agreement with other types of studies. Three interpretations have been proposed to explain the two-line or broad resonance associated with the Sn *DX* centers, the simplest of which requires a large lattice relaxation. A high-pressure Mössbauer experiment that should provide new information relevant to our proposed interpretations and to the issue of small versus large lattice relaxation is currently in progress.[59] In addition, x-ray-absorption spectroscopy experiments on Sn-doped $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ are underway.[60]

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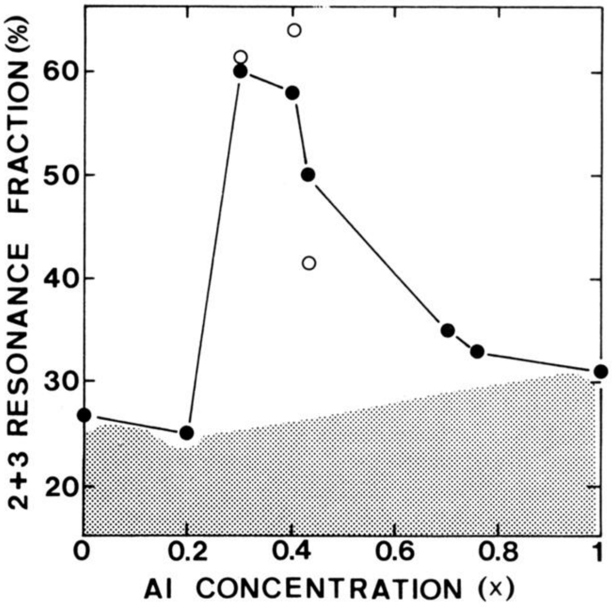

FIG. 3. Summed Mössbauer resonance fraction of lines 2 and 3 vs Al concentration. Solid circles from Table II. Open circles from Table III. Line is drawn to guide the eye. Region above shaded area is attributed to *DX* centers (see text).