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Experimental gradient-elastic tensors and chemical bonding in III-V semiconductors*

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Nuclear-acoustic-resonance determinations are made of the magnitudes and relative signs of the two different nonzero components S_{11} and S_{44} of the fourth-rank tensor relating electric field gradients to elastic strains. Measurements are made at 300 K and 10 MHz at the Al^{27} nuclear position in AlSb, at Ga^{69} in GaP, and at In^{115} in InP. Improved measurements are also made at the Ga^{69} nuclear position in GaAs and GaSb, at In^{115} in InAs and InSb, at As^{75} in InAs and GaAs, at Sb^{121} in AlSb, GaSb, and InSb. Theoretical S_{11} and S_{44} are computed assuming them to be sums of ionic and covalent contributions. Ionic contributions are approximated by point charges of the four first neighbors with effective charge Z^*. Covalent contributions are computed using atomic wave functions and bond polarity values α_p. Z^* and α_p are taken from Harrison's bond-optical model (BOM). Comparisons of theoretical and experimental S_{11} give (i) the sign of Z^* at the group-V atom as negative, (ii) agreement with the ratio of BOM values of Z^* in seven compounds, and (iii) signs and magnitudes of ionic and covalent contributions.

I. INTRODUCTION

Semiconducting crystals of III-V compounds have local T_d tetrahedral symmetry. At a nuclear position in the unstrained single crystal the electric field gradient will be zero. If elastic strain is introduced, there will now be nonzero electric field gradients at the nuclear positions due to changes in neighboring atom positions and in the chemical bonds. The electric-field-gradient relationship to the elastic strain can be written in terms of a tensor[1] of the fourth rank, S. From the crystal symmetry, there are three different nonzero components of S. When expressed in the Voigt notation, these are S_{11}, S_{12}, and S_{44}. We shall assume that the variation in the electric charge at the nuclear position with strain is zero.[2] This assumption results[2] in the relationship $S_{12} = -\frac{1}{2}S_{11}$.

In this paper, we report nuclear-acoustic-resonance (NAR) experimental determinations of S_{11} and S_{44} at the Al^{27} nuclear position in AlSb, at Ga^{69} in GaP, and at In^{115} in InP. We also report new, more accurate experimental determinations of S_{11} and S_{44} at the Ga^{69} nuclear position in GaAs and GaSb, at In^{115} in InAs and InSb, at As^{75} in GaAs and InAs, and at Sb^{121} in AlSb, GaSb, and InSb.

Point-charge and electronic contributions to S_{11} and S_{44} are computed and combined using the bond-orbital model of Harrison and Ciraci.[3] By comparing measured and computed values of S_{11} and S_{44}, it is possible to determine the sign of the effective ionic charge and the magnitudes of the point-charge and electronic contributions to S_{11}. In the remainder of the paper, we shall refer to the bond-orbital model as BOM and the Harrison and Ciraci paper as HC.

An initial NAR investigation of a III-V semiconductor was reported by Menes and Bolef[4] who determined the coupling of elastic waves to the In^{115} Sb nuclear-spin system as due to the dynamic quadrupole interaction. We used NAR to measure the S_{11} and S_{44} in five different III-V semiconductors in an earlier paper[5] which we shall call I. Other authors have employed nuclear magnetic resonance with static strain measurements,[6,7] and saturation experiments[8] to determine S_{11} and S_{44} for specific III-V compounds.

II. EXPERIMENTAL CONDITIONS AND DATA

A III-V-semiconductor sample

In Table I we give the physical properties and suppliers of the samples used in this investigation. All of the samples are intrinsic and were approximate cubes with a pair of (110) faces. The procedures used to determine these faces and the face preparation are described in I.

B. Experimental method

Nuclear-acoustic-resonance[9] experiments at 300 K were used to measure absolute values of the acoustic attenuation change due to absorption of resonant acoustic energy by a nuclear-spin system. One of the (110) faces of III-V compound single crystals was bonded with a 10-MHz *X*- or *AT*-cut fine ground quartz transducer. The combination of sample, bond, and transducer is called the composite resonator. Bonding of the transducer to the sample broadens the fundamental frequency response of the transducer. If the composite resonator is driven with an rf voltage near

TABLE I. III-V-semiconductor single-crystal samples. Physical properties determined by supplier.

Compound	Type	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Resistivity (Ω cm)	Etch-pit density (cm^{-2})
AlSb[a]	*p*	4×10^{16}	90	1.8	
GaP[b]	*n*	$2-30\times 10^{15}$	100		50 000
GaAs[c]	*n*	1.4×10^{16}	3 800	0.0115	1 200
GaSb[c]	*p*	1.7×10^{17}	570	0.066	5 000
InP[d]	*n*	$< 5\times 10^{17}$			
InAs[c]	*n*	1.4×10^{16}	18 200	0.024	1 100
InSb[c]	*p*	1.5×10^{16}	4 500	0.112	100

[a] Obtained from Bell and Howell Research Laboratories.

[b] Obtained from Metals Research LTD.

[c] Supplied by Monsanto Chemical Company.

[d] Obtained from Ministry of Technology, Electronic Materials unit, Royal Radar Establishment.

the fundamental frequency of the transducer, a large number of standing wave or mechanical resonances occur. The NAR experiment is performed by measuring the amplitude change of the one of these mechanical resonances as acoustic energy is absorbed by a nuclear-spin system under conditions of nuclear magnetic resonance.

In I we summarized the relationships between measured acoustic attenuation change and S_{11} and S_{44} when the nuclear-spin-acoustic-phonon coupling is via the dynamic quadrupole interaction. In the present experiments, only nuclear-spin transitions involving the nuclear-spin quantum number *m* changing by $\Delta m \pm 2$ were studied. This choice was made to take advantage of the narrower $\Delta m = \pm 2$ NAR linewidths.[10] We measure S_{44} by propagating transverse-acoustic waves at the Larmour frequency for $\Delta m = \pm 2$ transitions in the external magnetic field *H*. The propagation vector $\vec{k}$ was along [110], and the polarization vector $\vec{\xi}$ was along [001], $\vec{H}$ was in the (001) plane and ψ was the angle between $\vec{H}$ and $\vec{k}$. The attenuation change can be written

$$\Delta\alpha_{2x'z} = 4CB_2(QS_{44}\sin\psi)^2 \ . \tag{1}$$

We measured S_{11} by again using transverse-acoustic wave propagation with $\vec{k}$ along [110], $\vec{\xi}$ along [$1\bar{1}0$], $\vec{H}$ in the ($1\bar{1}0$) plane and χ as the angle between $\vec{H}$ and $\vec{k}$. The attenuation change is

$$\Delta\alpha_{2x'y'} = \tfrac{9}{4}\, CB_2(QS_{11}\sin\chi)^2 \ . \tag{2}$$

Relative signs between S_{11} and S_{44} were determined by propagating longitudinal-acoustic waves with $\vec{k}$ along [110] and $\vec{H}$ in the (001) plane. This attenuation change is

$$\Delta\alpha_{2x'x'} = CB_2Q^2(\tfrac{3}{4}S_{11} - S_{44}\cos 2\psi)^2 \ , \tag{3}$$

where

$$B_2 = \sum_m F_m(I)^2_{\pm 2} \ ,$$

$$F_m(I)_{\pm 2} = [(I \mp m)(I \mp m - 1)(I \pm m + 1)(I \pm m + 2)]^{1/2} \ ,$$

$$C = \frac{\pi^2}{16(2I)^2(2I-1)^2(2I+1)} \ \frac{N\nu^2 e^2 g(\nu)}{\rho v^2 kT} \ .$$

In the above expressions, *I* is the nuclear spin, *N* is the number of resonant nuclear spins per unit volume, ν is the elastic-wave frequency, $g(\nu)$ is the normalized line-shape function, ρ is the mass density, *v* is the acoustic-wave velocity, *k* is the Boltzmann constant, and *T* is the absolute temperature.

The procedures followed in the experiments described in this paper are identical with those of I with the following exceptions.

(i) The NMR calibrator[11] was located on the sample side of the NAR spectrometer. Such placement reduces the number of quantities to be measured in determining S_{11} and S_{44}.

(ii) Signal averaging with a Northern Scientific model 550 was used to achieve an output signal-to-noise ratio of greater than 100/1 for all nuclear-spin systems except $Al^{27}Sb$. A minimum time of 48 h of signal averaging was necessary to have a 5/1 signal-to-noise ratio with this nuclear-spin system.

(iii) All NAR analog data were digitized using the Northern Scientific 550. The line-shape factors of each nuclear-spin system except $Al^{27}Sb$ were determined by numerically integrating the experimental first derivative of the acoustic absorption signal. The $Al^{27}Sb$ signal-to-noise ratio was too small to determine an accurate line-shape factor. Since the experimental linewidths of $Al^{27}Sb$ and $AlSb^{121}$ were found to be identical, the $AlSb^{121}$ line-shape factor was used for $Al^{27}Sb$.

C. Experimental data

The magnitudes and relative signs of S_{11} and S_{44} were measured under the conditions describing Eqs. (1)–(3). Magnetic field modulation amplitudes were chosen to be no larger than one-eighth the experimental peak-to-peak NAR line shape. The dynamic elastic strain amplitudes were chosen to produce less than 1% saturation of the NAR signal. All NAR studies were made with $\vec{H}$ along $\langle 100\rangle$ directions where the effects of static quadrupole line broadening are minimum.[10] The magnitudes of S_{11} and S_{44} for each nuclear-spin system were measured on five different mechanical resonances. Each of the mechanical resonances could be described by a Lorentz line-shape function within experimental error.

In Table II we give the experimentally determined values of S_{11} and S_{44} with the quadrupole moments used in these determinations. The values of Table II are in good agreement with most previous S_{11} and S_{44} measurements in the III-V compounds. We find agreement within experimental errors between Table II and our earlier work I. We also find agreement of Table II In^{115} Sb values with those measured by static strain[6,7] and saturation.[8] However, there is disagreement between Table II values and the most recent static strain experiment[7] for GaSb, GaAs, AlSb, and InAs.

III. THEORY

We assume that the electric-field-gradient component V_{zz} can be written as the sum of two contributions: a point-charge or ionic contribution, and an electronic or covalent contribution. The field-gradient tensor components are expressed in orthogonal coordinates which are the principle axes of the tensor so that only diagonal components are different from zero. To be more specific, we write V_{zz} at a nuclear position in terms of its contributions from the charge distributions of the four nearest-neighbor atoms considered as point charges and from the bonding orbitals between the atom with nucleus at the origin and the four nearest neighbors.

$$V_{zz}=\sum_{i=1}^{4}\frac{(3\gamma_i^2-1)Z^*(1-\gamma_s)}{d^3}+\sum_{i=1}^{4}\frac{(-1)(3\gamma_i^2-1)}{2}\times 2e(1-R_s)\langle b|(3\cos^2\theta_i-1)/r_i^3|b\rangle\ . \tag{4}$$

In Eq. (4), γ_i is the direction cosine from the z principle axis to the ith bond direction, e is the electron-charge magnitude, Z^* is the effective ion charge of the nearest-neighbor atom (including sign of the charge), γ_s and R_s are the Sternheimer antishielding and shielding factors[12] for the solid, d is the nearest-neighbor distance, b is the bond-orbital wave function, and θ_i and r_i are the coordinates to the ith electron expressed with respect to an orthogonal coordinate system with its z axis along the ith bond direction. The factor $\frac{1}{2}(3\gamma_i^2-1)$ is due to the transformation of the electron part of V_{zz} from a coordinate system with z axis along the ith bond direction to the z direction of the principal axes. The factor of 2 in the electronic part comes from assuming two electrons per bond, and the minus sign is from the field-gradient definition.[13]

The Sternheimer term $1-\gamma_s$ is introduced[12,13] to correct V_{zz} at a nuclear position of an ion due to the interaction of the ion with its nuclear quadrupole moment and with the external point-charge electric field gradient. The term $1-R_s$ is a shielding correction to account[12,13] for the shielding effect of the core electrons in the atom whose nucleus is at the coordinate origin.

For zero strain, we expect V_{zz} to be zero. The coupling between acoustic waves and the nuclear-spin system in an NAR experiment[9] involves a linear dependence of field gradient on strain. By expanding Eq. (4) in a Taylor series in a specific component of strain, we can identify S_{11} and S_{44} as the expansion coefficients which are linear in strain. The component S_{11} is found by taking V_{zz} along a [001] crystal direction and choosing a component of strain $e_{zz}=\partial u_z/\partial z$ along the same direction. We write the z displacement $u_z=ze_{zz}$. The component S_{44} is found by choosing $V_{z'z'}$ along a [110] direction and choosing a component of

TABLE II. Experimentally determined components of S and quadrupole moments used in their calculation. The quadrupole moments are expressed with atomic shielding corrections made and are in units of $10^{-24}\,\mathrm{cm}^2$. Components S_{11} and S_{44} have units of 10^{+15} statcoulomb cm^{-3}. The experimental uncertainty of QS_{11} or QS_{44} is ±10% for Al^{27}, ±6% for Ga^{69}, and 4% for In^{115}, As^{75}, and Sb^{121}.

Nucleus	Compound	Q	S_{44}	S_{11}
Al^{27}	AlSb	0.165 ± 0.003[a,b]	±3.8	∓2.6
Ga^{69}	GaP	0.199 ± 0.001[b]	±8.2	∓9.5
Ga^{69}	GaAs	0.199 ± 0.001	±9.2	∓9.1
Ga^{69}	GaSb	0.199 ± 0.001	±8.1	∓6.1
In^{115}	InP	0.860 ± 0.001[b]	±8.7	∓19.7
In^{115}	InAs	0.860 ± 0.001	±10.0	∓16.7
In^{115}	InSb	0.860 ± 0.001	±10.5	∓13.1
As^{75}	GaAs	0.27 ± 0.04[c]	±26.5	±13.2
As^{75}	InAs	0.27 ± 0.04	±25.2	±13.0
Sb^{121}	AlSb	0.53 ± 0.08[d]	±31.4	±13.5
Sb^{121}	GaSb	0.53 ± 0.08	±31.5	±10.7
Sb^{121}	InSb	0.53 ± 0.08	±30.0	±12.3

[a] H. Low and G. Wessel, Phys. Rev. 90, 1 (1953).

[b] G. F. Koster, Phys. Rev. 86, 148 (1952).

[c] K. Murakawa, Phys. Rev. 110, 393 (1958).

[d] K. Murakawa, Phys. Rev. 100, 1369 (1955).

strain e_{xy} where x is along [100] and y along [010]. We write $e_{xy} = (\partial u_x/\partial y) + (\partial u_y/\partial x)$ where $u_x = ye_{xy}$ and $u_y = xe_{xy}$.

One set of first neighbors has the coordinates relative to the crystal axes $(d/\sqrt{3})(1, 1, 1)$, $(d/\sqrt{3})(-1, -1, 1)$, $(d/\sqrt{3})(-1, 1, -1)$, and $(d/\sqrt{3})(1, -1, -1)$. We resolve the strain component which defines S_{11}, namely e_{zz}, into radial displacements along bond directions and angular displacements perpendicular to bond directions. Because of the strain direction relative to first-neighbor directions, only angular changes in bond directions contribute to S_{11}.

As discussed by HC, the pure shear e_{xy} will cause an inner displacement[14] of the anion sublattice relative to the cation sublattice. Such an inner displacement causes a displacement of the nearest neighbor in the z direction

$$u_z = -\xi d e_{xy}/\sqrt{3} \ , \tag{5}$$

where ξ is Kleinman's[15] inner displacement parameter which has been calculated by Martin[16] from fitting force constants to measured elastic constants. The strain e_{xy} which defines S_{44} will give both angular and radial contributions.

A. Point-charge contribution

As in I, the field gradient is computed from each successive shell of atoms at constant distance r from a nuclear position. The charge distribution at each neighboring ion is regarded as a point charge Z^*. The contributions from first through twenty-fifth shells have been computed directly. As pointed out by Cohen and Reif,[13] the largest contribution is from the four first neighbors. We expect that ionic contributions from the second or third shells and further shells should be scaled by the static microscopic dielectric constant to approximate the electronic screening. On the other hand, in these near intrinsic semiconductors with very small conduction-band populations, we expect little screening for the first-neighbor shell charges. Therefore, we assume a step dielectric function so that point charges of the first neighbors are not screened, but those from second and the remaining shells are screened. Because of the large static microscopic dielectric constants[17] of the III-V compounds, the point-charge contributions to the electric field gradient become those of the first neighbors.

The effective charge of the anion, Z_a^*, is defined by HC to be

$$Z_a^* = -(4\alpha_p - 1)e \tag{6}$$

for III-V compounds. The polarity α_p is determined from two of the three basic parameters of the BOM. The change in α_p due to an increase in bond length Δd is[2]

$$\Delta\alpha_p = s\alpha_p(1 - \alpha_p^2)\Delta d/d \ , \tag{7}$$

where s is shown by HC to be close to 2. We take $s = 2$ in this paper. The point-charge contributions at the anion nuclear position to S_{11} and S_{44} become

$$S^a_{11\,\mathrm{ionic}} = \tfrac{16}{3}(Z_c^*/d^3)(1 - \gamma_s) \ , \tag{8}$$

$$S^a_{44\,\mathrm{ionic}} = \left(\tfrac{3}{4} - \tfrac{5}{4}(1 - \xi) + (1 - \xi)\,\frac{2\alpha_p(1 - \alpha_p^2)}{Z_c^*/e}\right) S^a_{11\,\mathrm{ionic}} \ , \tag{9}$$

and at the cation nuclear position

$$S^c_{11\,\mathrm{ionic}} = \tfrac{16}{3}(Z_a^*/d^3)(1 - \gamma_s) \ , \tag{10}$$

$$S^c_{44\,\mathrm{ionic}} = \left(\tfrac{3}{4} - \tfrac{5}{4}(1 - \xi) - (1 - \xi)\,\frac{2\alpha_p(1 - \alpha_p^2)}{Z_a^*/e}\right) S^c_{11\,\mathrm{ionic}} \ . \tag{11}$$

B. Bond contribution

We use the BOM to describe the molecular bond. The bond is constructed from sp^3 hybrids. For an orthogonal coordinate system with origin at an anion nuclear position and with z axis along a bond-orbital axis, the hybrid on the anion can be written as

$$|h^a\rangle = \tfrac{1}{2}(|s^a\rangle + \sqrt{3}\,|p^a\rangle) \ , \tag{12}$$

and the hybrid on the cation as

$$|h^c\rangle = \tfrac{1}{2}(|s^c\rangle - \sqrt{3}\,|p^c\rangle) \ . \tag{13}$$

The molecular bond with origin at the anion nuclear position is

$$|b^a\rangle = u_a|h^a\rangle + u_c|h^c\rangle \ . \tag{14}$$

By minimizing the bond energy, HC find

$$u_a^2 = \tfrac{1}{2}\left(\frac{1 - S(1 - \alpha_p^2)^{1/2}}{1 - S^2} + \frac{\alpha_p}{(1 - S^2)^{1/2}}\right) \ , \tag{15}$$

$$u_c^2 = \tfrac{1}{2}\left(\frac{1 - S(1 - \alpha_p^2)^{1/2}}{1 - S^2} - \frac{\alpha_p}{(1 - S^2)^{1/2}}\right) \ , \tag{16}$$

where $S = \langle h^a | h^c \rangle$. We define $q = (3\cos^2\theta_i - 1)/r_i^3$ and write the bond-orbital expression in Eq. (4) as

$$\langle b^a|q^a|b^a\rangle = u_a^2\langle h^a|q^a|h^a\rangle + 2u_a u_c\langle h^a|q^a|h^c\rangle + u_c^2\langle h^c|q^a|h^c\rangle \ . \tag{17}$$

Because of the orthogonality of the atomic orbitals s^a and p^a, the first term of the right-hand side of Eq. (17) is $\frac{3}{4}u_a^2\langle p^a|q^a|p^a\rangle$. In order to estimate the magnitudes of the contributions to the electric field gradient from the integrals $q^a_{zz} = \langle p^a|q^a|p^a\rangle$, $q^a_{ac} = \langle h^a|q^a|h^c\rangle$, $q^a_{cc} = \langle h^c|q^a|h^c\rangle$, and S and similar integrals at the cation nuclear position, bond orbitals

TABLE III. Values of $\langle r^{-3}\rangle$ for specific atoms having p electrons. The quantity $\langle r^{-3}\rangle$ is expressed in atomic units.

Atom	Hartree-Fock[a] numerical	Hartree-Fock[b] analytic	Barnes and Smith[c]
Al	1.0883	1.0855	1.27
P	3.2667	3.3002	3.48
Ga	4.8908	2.865	3.51
As		6.879	7.46
In	4.4572	4.312	5.72
Sb	9.2313	9.045	13.03

[a] See Refs. 12 and 20.
[b] This paper.
[c] See Ref. 21.

TABLE IV. Values of the overlap integral S and the change in S with bond-length change, $\Delta S=(\partial S/\partial r)d_{r=d}$.

Nuclear position	S	ΔS
$\mathrm{Al}^{27}\mathrm{Sb}$	0.659	−0.582
$\mathrm{Ga}^{69}\mathrm{P}$	0.627	−0.392
$\mathrm{Ga}^{69}\mathrm{As}$	0.635	−0.456
$\mathrm{Ga}^{69}\mathrm{Sb}$	0.657	−0.530
$\mathrm{In}^{115}\mathrm{P}$	0.600	−0.411
$\mathrm{In}^{115}\mathrm{As}$	0.611	−0.480
$\mathrm{In}^{115}\mathrm{Sb}$	0.642	−0.536
GaAs^{75}	0.635	−0.458
InAs^{75}	0.611	−0.479
AlSb^{121}	0.659	−0.483
GaSb^{121}	0.657	−0.491
InSb^{121}	0.642	−0.535

were approximated by linear combinations of atomic orbitals (LCAO). We assumed that only the valence shell electrons contribute to the bonding orbitals and that these orbitals can be written as LCAO of Hartree-Fock atomic orbitals for neutral ground-state atoms. Recently, computed atomic orbitals of Roetti and Clementi[18] were used. Two center integrals were computed using a ζ function expansion procedure due to Barnett and Coulsen.[19] Computations were done using FORTRAN IV coding on a Digital Equipment Corporation PDP 11 disk operating system. The change in the two center integrals with change in bond length was also studied.

Table III contains values of $\langle 1/r^3\rangle=\frac{5}{4}q_{zz}$ which we have computed using the analytic Hartree-Fock functions, results of computations by Froese[12,20] for numerical Hartree-Fock functions, and values computed by Barnes and Smith[21] from the experimental fine-structure splitting of the optical lines due to the spin-orbit interaction. Table III shows good agreement among the values except for Ga and Sb. Values of the overlap integral S and the change in S, $\Delta S=(\partial S/\partial r)_{r=d}\,d$ with bond-length change Δd are given in Table IV. The values of S in Table IV are approximately 10% smaller than those computed by Hüber[22] using Slater wave functions. Pruitt, Marshall, and O'Donnell[23] have computed $S\simeq 0.5$ for AlSb, GaSb, and InSb. Using atomic orbitals appropriate to the solid, HC compute $S=0.5$ for Si.

The LCAO calculations gave values for q_{ac} and the change in q_{ac} with bond-length change that are less than 1% of q_{zz}. The values of q_{cc}^{a} cannot be determined accurately because of differencing effects[19] in the application of the Barnett and Coulsen method. We estimate that q_{cc}^{a} is also less than 1% of q_{zz}.

On the basis of the above LCAO calculations, we expect that radial contributions to the covalent part of S_{44} will come only from changes in the electron probability terms u_a^2 and u_c^2 with bond-length change. Changes in these terms will involve changes of the overlap S and the polarity α_p with bond-length change. The covalent contributions to S_{11} and S_{44} at the anion nuclear position can be written

$$S^{a}_{11\,\mathrm{cov}}=-\tfrac{16}{5}u_a^2\,e\langle r^{-3}\rangle_a(1-R_s)_a\ , \tag{18}$$

$$S^{a}_{44\,\mathrm{cov}}=-\tfrac{1}{4}[3-2(1-\xi)+(1-\xi)(\Delta u_a^2/u_a^2)]S^{a}_{11\,\mathrm{cov}}\ , \tag{19}$$

where $\Delta u_a^2=(\partial u_a^2/\partial r)_{r=d}\,d$. The expressions for the cation nuclear position are identical with the subscripts or superscripts a being replaced by c.

TABLE V. Quantities used in computing the ionic and covalent contributions to S_{11}. The polarity α_p, polarity change with bond extension $\delta\alpha_p=2\alpha_p(1-\alpha_p^2)$, and effective charge at the cation Z^*, are computed from the BOM theory. The ionic term e/d^3 has units 10^{15} statcoulomb cm^{-3} and $1-\gamma_\infty$ is the Sternheimer antishielding factor for the free atom.

Nuclear position	α_p	$\delta\alpha_p$	Z^*/e	e/d^3[d]	$1-\gamma_\infty$	ξ[e]
$\mathrm{Al}^{27}\mathrm{Sb}$	0.541	0.765	1.16	0.025 61	2.5[a]	0.65
$\mathrm{Ga}^{69}\mathrm{P}$	0.522	0.760	1.09	0.036 53	10.5[b]	0.59
$\mathrm{Ga}^{69}\mathrm{As}$	0.490	0.745	0.96	0.032 74	10.5[b]	0.60
$\mathrm{Ga}^{69}\mathrm{Sb}$	0.435	0.705	0.74	0.026 12	10.5[b]	0.61
$\mathrm{In}^{115}\mathrm{P}$	0.582	0.770	1.33	0.029 25	25.9[c]	0.70
$\mathrm{In}^{115}\mathrm{As}$	0.530	0.762	1.12	0.026 61	25.9[c]	0.68
$\mathrm{In}^{115}\mathrm{Sb}$	0.510	0.784	1.04	0.021 76	25.9[c]	0.70

[a] See Ref. 24.
[b] See Ref. 25.
[c] See Ref. 26.
[d] G. Giesecke and H. Pister, Acta Crystallegr. 11, 369 (1958).
[e] See Ref. 16.

IV. ANALYSIS AND DISCUSSION

We have described in Sec. III a theoretical model which interprets the measured S_{11} and S_{44} values as sums of ionic and covalent contributions. To approximate the ionic contribution to S_{11} and S_{44} in Eqs. (8)–(11), we use the BOM value for effective charge Z^* and use the calculated atomic value of $1-\gamma_\infty$ for $1-\gamma_s$. Computed atomic antishielding factors depend on the charge of the ion,[24] especially for the small atomic number Al ion. We choose a value of $1-\gamma_\infty$ for Al corresponding to Z^* extrapolating between computed values[24] of $1-\gamma_\infty$ for Al^+ and Al^{2+}. For the two other metal ions, the $1-\gamma_\infty$ is chosen to be the computed values[25,26] for Ga^{3+} and In^{3+}. No computed values of $1-\gamma_\infty$ for As and Sb have been found. The values of Z^* and $1-\gamma_\infty$ chosen are listed in Table V.

For the covalent contributions to S_{11} and S_{44}, Eqs. (18) and (19), we use the Barnes and Smith[21] values of $\langle r^{-3}\rangle$ for free atoms and assume $R_s = 0$. The electron probability terms u_a^2 and u_c^2 are determined using values of α_p computed from the BOM and values of overlap S from Table IV. Table V lists the computed values of α_p and Table VI values of u_a^2 and u_c^2.

The ionic and covalent contributions to S_{44}, Eqs. (9), (11), and (19) involve in addition to the previously discussed variables the changes in α_p and overlap S with bond-length change and Kleinman's inner displacement parameter ξ. Computed values of $2\alpha_p(1-\alpha_p^2)$ and Martin's values[16] for ξ are given in Table V and values of ΔS are given in Table IV.

As noted in Sec. III, the component of strain e_{zz} which defines S_{11} involves only angular changes in the charge distributions and the bonding orbitals to the four first-neighbor atoms. It is this independence of bond-length change which makes the expressions for S_{11}, Eqs. (8), (10), and (18) much simpler than those for S_{44}, Eqs. (9), (11), and (19).

TABLE VI. Comparison of computed covalent contributions to S_{11} where the metallic atom is considered to be an anion and a cation. Predicted ionic contributions to S_{11} are determined from the computed covalent contributions and the measured S_{11} values. The units of S_{11} are 10^{15} statcoulomb cm^{-3}.

Nuclear position	u_a^2	u_c^2	$S_{11\,\mathrm{cov}}^a$	$S_{11\,\mathrm{cov}}^c$	$S_{11\,\mathrm{ionic}}^a$	$S_{11\,\mathrm{ionic}}^c$
$Al^{127}Sb$	0.691	0.0294	−9.1	−0.388	−6.5	−2.2
$Ga^{69}P$	0.718	0.0483	−26.1	−1.75	+16.6	−7.7
$Ga^{69}As$	0.691	0.0569	−25.2	−2.07	+16.1	−7.0
$Ga^{69}Sb$	0.648	0.0708	−23.6	−2.58	+17.5	−3.52
$In^{115}P$	0.764	0.0363	−45.3	−2.15	+25.6	−17.6
$In^{115}As$	0.719	0.0500	−42.7	−2.97	+26.0	−13.7
$In^{115}Sb$	0.713	0.0483	−42.3	−2.87	+29.2	−10.2

TABLE VII. Comparison of ionic contributions to S_{11} determined two different ways. $S_{11\,\mathrm{ionic}}^c$ is computed from the covalent contribution to S_{11} and the experimental S_{11} and is taken from Table VI. The quantity $A_{\mathrm{ionic}} = -\frac{16}{3}Z^*(1-\gamma_\infty)d^{-3}$ is computed from the ionic model. The prouct fA_{ionic}, where $f = S_{11\,\mathrm{ionic}}^c(\mathrm{InP})/A_{\mathrm{ionic}}(\mathrm{InP}) = 3.3$ is compared with $S_{11\,\mathrm{ionic}}^c$ for seven compounds. A_{ionic} and $S_{11\,\mathrm{ionic}}^c$ are in units 10^{15} statcoulombs cm^{-3}.

Nuclear position	A_{ionic}	$S_{11\,\mathrm{ionic}}^c$	fA_{ionic}
$Al^{27}Sb$	−0.39	−2.2	−1.28
$Ga^{69}P$	−2.23	−7.7	−7.31
$Ga^{69}As$	−1.76	−7.0	−5.77
$Ga^{69}Sb$	−1.08	−3.52	−3.53
$In^{115}P$	−5.37	−17.6	−17.6
$In^{115}As$	−4.11	−13.7	−13.5
$In^{115}Sb$	−3.13	−10.2	−10.3

A. S_{11} for group-III atoms; sign of Z_V^*

We first will use the experimental S_{11} values at group-III atom nuclear positions with the BOM to determine the sign for the group-V atom effective charge Z_V^*. The sign of the covalent contribution to S_{11} in Eq. (18) is negative. The sign of the experimental S_{11} is not determined; only the relative sign between S_{11} and S_{44} is measured. We compute the covalent contributions to S_{11} and assume first that the group-III atom is an anion and then a cation. Because of the much smaller computed values of u_c^2 than u_a^2, the computed values of $S_{11\,\mathrm{cov}}^c$ are much smaller than $S_{11\,\mathrm{cov}}^a$ as shown in columns 4 and 5 of Table VI. If the group-III atom were an anion, then Z_V^* would be positive. Therefore, we chose the sign of the experimental S_{11} to make $S_{11\,\mathrm{ionic}}^a = S_{11} - S_{11\,\mathrm{cov}}^a > 0$. Values of $S_{11\,\mathrm{ionic}}^a$ are shown in column 6 of Table VI. If the group-III atom were a cation, then Z_V^* would be negative. Now the sign of the experimental S_{11} is chosen to make $S_{11\,\mathrm{ionic}}^c = S_{11} - S_{11\,\mathrm{cov}}^c < 0$. Values of $S_{11\,\mathrm{ionic}}^c$ are given in column 7 of Table VI. If the subtracted value $S_{11\,\mathrm{ionic}}^a$ or $S_{11\,\mathrm{cov}}^c$ is the proper ionic contribution, it should vary at the same nuclear position in different compounds as Z_V^*/d^3. Comparing columns 6 and 7 of Table VI with column 2 of Table VII, we find agreement between $S_{11\,\mathrm{ionic}}^c$ and A_{ionic} and disagreement between $S_{11\,\mathrm{ionic}}^a$ and A_{ionic}. Furthermore, the incorrect sign is predicted for $S_{11\,\mathrm{ionic}}^a$ of Al in column 6 of Table VI. We conclude that the correct identification of signs of effective charges is $Z_a^* = Z_V^* < 0$ and $Z_c^* = Z_{III}^* > 0$.

In column 2 of Table VII, we have computed A_{ionic} from Eq. (8) as the ionic contribution. In column 3 of Table VII, we rewrite the value $S_{11\,\mathrm{ionic}}^c$ determined from the measured S_{11} and computed $S_{11\,\mathrm{cov}}^c$. By picking one compound, such as

InP, and multiplying the ratio $(S^c_{11\,\text{ionic}}/A_{\text{ionic}})_{\text{InP}}=f$ times the other values of A_{ionic}, close agreement results between fA_{ionic} in column 3 and $S^c_{11\,\text{ionic}}$ in column 4 of Table VII. This good agreement over seven compounds is related to the BOM prediction of small $S^c_{11\,\text{cov}}$. Changing the value of overlap S to 0.5 for each compound increases u_a^2 by a factor of approximately 2. Such a change in u_c^2 does not alter the presence of a common ratio f between $S^c_{11\,\text{ionic}}$ and A_{ionic}. If the shielding constant R_s is assumed not to be zero, but to have a value between 0 to 1, then an even smaller value of S^c_{11} would result.

The common ratio of $S^c_{11\,\text{ionic}}$ to A_{ionic} over seven compounds supports the BOM predictions of Z^* for these seven compounds. The larger value of $S^c_{11\,\text{ionic}}$ than A_{ionic}, $f=3.3$ in Table VII, cannot be explained by including more neighboring atomic shells in the computation of A_{ionic}. If, for example, there was no electronic screening of point ions in first-, second-, and third-neighbor shells of atoms, the numerical constant in A_{ionic} would be smaller. If the description of the ionic model leading to Eq. (8) and A_{ionic} were correct, then it would follow that $(1-\gamma_s)/(1-\gamma_\infty)=f=3.3$ for all seven compounds.

B. S_{11} at group-V nuclear positions

We do not know the atomic antishielding factors for the group-V atoms, but we can compute the covalent contributions to S_{11} assuming $R_s=0$. The values of u_a^2 in Table VI have been used to compute $S_{11\,\text{cov}}$ which is listed for five compounds in column 2 of Table VIII. Because of the larger $\langle r^{-3}\rangle$ for As and Sb and the larger u_a^2 than u_c^2, values of $S_{11\,\text{cov}}$ at the anion nuclear positions are much larger than such values at the cation nuclear positions.

The $S_{11\,\text{ionic}}$ values at group-V nuclear positions must be positive if $Z^*_{\text{III}}=Z^*_c>0$. We choose the sign of the measured S_{11} to be negative; this choice results in the smaller of two positive values for $S_{11\,\text{ionic}}$. The values of $S_{11\,\text{ionic}}$ are listed in column 3 of Table VIII. In column 4 of Table VIII we list computed values of $A_{\text{ionic}}/(1-\gamma_\infty)=\frac{16}{3}Z^*/d^3$.

The experimental S_{11} values of Table IV at group-III nuclear positions are in agreement with the model described in Sec. III and the BOM. The experimental S_{11}, $S_{11\,\text{cov}}$, $S_{11\,\text{ionic}}$, and $A_{\text{ionic}}/(1-\gamma_s)$ all have, within 6%, the same values at GaAs^{75} and InAs^{75}. The constant value of $A_{\text{ionic}}/(1-\gamma_\infty)$ is due to the BOM prediction of the ratio $Z^*_{\text{GaAs}}/Z^*_{\text{InAs}}$ which has approximately the same value as $d^{-3}_{\text{GaAs}}/d^{-3}_{\text{InAs}}$. The values of the experimental S_{11}, $S_{11\,\text{cov}}$, $S_{11\,\text{ionic}}$, and A_{ionic} all have magnitudes at the Sb nuclear position which follow the inequality AlSb > InSb > GaSb. This ordering disagrees with that predicted on the basis of Mössbauer isomer shift measurements[23] on AlSb, GaSb, and InSb.

The assumption $R_s=0$ has been made in the determination of $S_{11\,\text{cov}}$. If the shielding factor at group-V atom nuclear positions is not zero, then the computed $S_{11\,\text{cov}}$ and $S_{11\,\text{ionic}}$ would be smaller. With the assumption $R_s=0$, $(1-\gamma_s)$ is required to be approximately 240 for As and 700 for Sb.

C. S_{44} components

The experimental S_{44} values in Table II show little variation at the same nuclear position in different compounds. At the Ga nuclear position, the change in S_{44} in three compounds is 12%, at In 17%, at As 5%, and at Sb 5%. Table II also shows the experimental S_{44} to have opposite signs from the experimental S_{11} at group-III nuclear positions and identical signs at group-V nuclear positions. On the basis of the identifications of signs of S_{11} above, we expect that $S_{44}>0$ at group-III nuclear positions and that S_{44} could be either positive or negative at group-V nuclear positions depending on the magnitude of $S_{11\,\text{ionic}}$.

When we apply the BOM to explain the experimental S_{44} values, we find the predicted S_{44} to have a negative sign and to be only 50% of the experimental S_{44} for group-V nuclear positions. The predicted S_{44} at group-III nuclear positions has the incorrect sign. The method applied in computing the predicted S_{44} values was to use $S_{11\,\text{cov}}$ and $S_{11\,\text{ionic}}$ from Tables VI–VIII and Eqs. (9), (11), and (19). Kleinman's inner displacement term ξ is estimated[16] to have a 20% error. However, by allowing ξ to take any value between 0 and 1 does not produce agreement with the experimental S_{44}. We conclude that Eq. (19) is probably missing one or more terms which describe the covalent contribution to the field gradient due to bond-length change.

V. SUMMARY

(i) Experimental determinations of S_{11} and S_{44} have been made at three different group-III-atom nuclear positions and at two different group-V-atom nuclear positions in a series of seven III-V compounds.

(ii) A theoretical model is proposed to explain S_{11} and S_{44} values which uses BOM predictions of effective charge Z^* and description of the molecular bond, atomic values for $\langle r^{-3}\rangle$ and $1-\gamma_\infty$, LCAO computed values for overlap S and ΔS, and computed values[16] of Kleinman's inner displacement parameter.

(iii) Use of the BOM allows computation of the covalent contribution to S_{11} at group-III nuclear

TABLE VIII. Computations of covalent contributions to S_{11} at the nonmetal nuclear positions and estimates of the ionic contributions. $S_{11\,\mathrm{cov}}$ and $S_{11\,\mathrm{ionic}}$ are in units 10^{15} statcoulomb cm^{-3}.

Nuclear position	$S_{11\,\mathrm{cov}}$	$S_{11\,\mathrm{ionic}}$	$A_{\mathrm{ionic}}/(1-\gamma_\infty)$
GaAs^{75}	−53.5	+40.3	0.167
InAs^{75}	−55.7	+42.7	0.159
AlSb^{121}	−101.9	+88.4	0.159
GaSb^{121}	−87.6	+76.9	0.103
InSb^{121}	−96.5	+84.2	0.121

positions. The ionic contributions determined by subtracting the covalent contributions to S_{11} from the experimental S_{11} are in agreement with the ionic contribution computed from the BOM effective charges and the point-charge model only if $Z_V^* = Z_a^* < 0$. The ratio of the two ionic contributions, with the inclusion of atomic antishielding factors in the point-charge terms, is approximately constant for the seven compounds. This common ratio shows agreement of the interpreted data with the BOM values of Z^*. The lack of agreement of the two ionic magnitudes can be interpreted as indicating $1-\gamma_s > 1-\gamma_\infty$. The experimental S_{11} are found to have negative signs and to have large negative ionic contributions and small negative covalent contributions.

(iv) At group-V nuclear positions, the covalent contribution to S_{11} is computed, subtracted from the experimental S_{11} to determine the ionic contribution to S_{11}. With the assumption of the shielding constant $R_s = 0$, one finds a large negative covalent contribution and a large positive ionic contribution. The sign of the experimental S_{11} depends on which of the two contributions is larger. Antishielding factors necessary to explain the magnitude of the ionic contributions are approximately 240 at the As nuclear position and 700 at Sb. If the shielding constant were between 0 and 1, smaller covalent and therefore smaller ionic contributions would result.

(v) With values of overlap of $S = 0.5-0.7$, the BOM values of u_c^2 are small and those of u_a^2 are large. This difference is responsible for the small covalent contributions to S_{11} at group-III nuclear positions and the large values at group-V nuclear positions. Such differences in ionic and covalent contributions at group-III and group-V nuclear positions may prove useful in explaining the differences in nuclear magnetic resonance spin-lattice relaxation time measurements[27,28] at group-III and group-V nuclear positions.

(vi) Predicted S_{11} values are much easier to estimate than S_{44} values. With the assumption of only first-neighbor contributions, the predicted S_{11} involve only angular changes in first-neighbor positions while the predicted S_{44} involves both angular and radial changes in first-neighbor positions. Changes in bond length were assumed due to changes in overlap S and change in polarity α_p. The introduction of Kleinman's inner displacement parameter in the description of S_{44} further complicates its determination. The result that the predicted and experimental S_{44} values do not agree is therefore not surprising. This lack of agreement may also be due to a missing term in the covalent contribution due to changes in the bonding orbital with bond extension.

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