

# Pressure-induced changes in the electronic structure of arsenic and antimony metal

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The pressure dependence of nuclear spin lattice relaxation (NSLR) in semimetallic arsenic (0–2 GPa) and antimony (0–1.4 GPa) at ambient temperature has been investigated by means of  $^{75}\text{As}$ ,  $^{121}\text{Sb}$ , and  $^{123}\text{Sb}$  nuclear quadrupole resonance (NQR). Previous investigations indicate that relaxation in these materials is dominated by magnetic nucleus–carrier interactions. NSLR measurements therefore provide information on the carrier and Fermi surface properties. Our results indicate that antimony becomes more metallic under pressure, while arsenic becomes less metallic. This is consistent with previous experimental and theoretical results. The NQR measurements are, in particular, sensitive to changes in the  $s$ -wave character of the carriers. The NQR results are compared with previous experimental and theoretical studies of the electronic structure of the Group V semimetals.

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## I. INTRODUCTION

The electronic structure (ES) of the Group V semimetals (arsenic, antimony, and bismuth) has received considerable attention from both theorists and experimentalists in the past<sup>1</sup> due to the interesting position these materials occupy between metals and semiconductors. The crystal structure of the Group V semimetals is a slight rhombohedral ( $A7$  structure,  $R\bar{3}m$  point group) distortion from cubic symmetry, and leads to a Fermi surface consisting of small electron and hole pockets. The ES is expected to depend sensitively on the lattice parameters, and pressure-induced changes in the electronic properties are, therefore, of interest. In particular, the pressure dependence of the ES has been studied experimentally using transport measurements (0–8 GPa in antimony,<sup>2</sup> 0–12 GPa in arsenic<sup>3</sup>), the de Haas–van Alphen effect (0.2–0.8 GPa in antimony<sup>4</sup>), and more recently nuclear quadrupole resonance (NQR) (0–1 GPa in arsenic<sup>5</sup>). Theoretical studies of the pressure dependence of the ES have been carried out using pseudopotential techniques.<sup>6,7</sup> Recent developments in density functional theory utilizing full-potential linearized augmented plane wave (FLAPW) techniques<sup>8</sup> have made it possible to calculate some features of the ES and the carrier wave functions more accurately than was previously possible.

In this paper we present pulsed NQR measurements of the nuclear spin-lattice relaxation (NSLR) rates as a function of pressure at ambient temperature for arsenic and antimony up to a maximum pressure of 2.0 GPa. Fermi surface parameters and information on the carrier wave functions have been inferred from the NSLR data. These results are compared to previous experimental and theoretical work, and should provide a useful comparison for modern theoretical treatments of the electronic structure of the Group V semimetals.

## II. THEORETICAL CONSIDERATIONS

The energy levels resulting from the interaction between an axially symmetric electric field gradient (efg), as appropriate for the lattice structure of arsenic and antimony, and

the quadrupole moment  $Q$  of a nucleus are given by

$$E_{\pm m} = \frac{e^2 q Q}{4I(2I-1)} [3m^2 - I(I+1)]. \quad (1)$$

Here,  $eq$  is the component of the efg tensor along the axis of symmetry of the crystal,  $I$  is the nuclear angular momentum quantum number, and  $m$  is the quantum number for  $I_z$ . The energy levels are degenerate for  $\pm m$ . The three naturally occurring isotopes in arsenic and antimony are  $^{75}\text{As}$  ( $I = \frac{3}{2}$ , 100% abundant),  $^{121}\text{Sb}$  ( $I = \frac{5}{2}$ , 57.25% abundant), and  $^{123}\text{Sb}$  ( $I = \frac{7}{2}$ , 42.75% abundant). All three isotopes were studied in this work.

Full relaxation equations describing NSLR for any of the transitions in a quadrupolar system may be derived in terms of the magnetic ( $\Delta m = \pm 1$ ) and quadrupolar ( $\Delta m = \pm 1, \Delta m = \pm 2$ ) transition probabilities.<sup>9</sup> In the case that magnetic interactions dominate, these simplify to the following three equations:

$$u_{3/2}(t) = 2\nu e^{-6W_m t}, \quad (2)$$

$$u_{5/2}(t) = \frac{2\nu}{7} [3e^{-6W_m t} + 4e^{-20W_m t}], \quad (3)$$

$$u_{7/2}(t) = \frac{\nu}{77} [33e^{-6W_m t} + 100e^{-20W_m t} + 21e^{-42W_m t}], \quad (4)$$

for the  $^{75}\text{As}$  ( $\frac{3}{2} \leftrightarrow \frac{1}{2}$  transition),  $^{121}\text{Sb}$  ( $\frac{5}{2} \leftrightarrow \frac{3}{2}$  transition), and  $^{123}\text{Sb}$  ( $\frac{7}{2} \leftrightarrow \frac{5}{2}$  transition) nuclei, respectively. The quantity  $\nu$  depends on experimental conditions, and describes the disturbance from equilibrium of the nuclear spin system, and  $W_m$  is the magnetic relaxation rate.

Previous NQR measurements<sup>10–12</sup> show Korringa NSLR ( $W_m/T = \text{constant}$ ) at low temperatures, followed by a quadratic increase in the relaxation rate beyond the Debye temperature in both arsenic ( $\Theta_D = 280$  K) and antimony ( $\Theta_D = 210$  K). The Korringa behavior indicates that, at low temperatures, nuclear spin-lattice interactions in these materials are dominated by magnetic interactions between the nuclear

spins and the carriers at the Fermi surface. Later measurements<sup>9</sup> employed a two-isotope technique in order to separate magnetic and quadrupolar contributions to NSLR in antimony over the temperature range 4.2–435 K. While these measurements do indicate an increase in the relative quadrupolar contribution to NSLR in the vicinity of the Debye temperature, this contribution remains smaller than 2% over the full temperature range studied. The deviation from Korringa behavior is, therefore, predominantly magnetic in origin, signaling temperature-induced changes in the Fermi surface properties of antimony.<sup>9</sup> The increase in the quadrupolar transition rates in the region of  $\Theta_D$  may indicate the onset of a Raman nucleus-phonon mechanism.<sup>13</sup>

The two-isotope measurements described previously indicate that, at room temperature, quadrupolar interactions can be ignored in antimony, and the magnetic transition rates for <sup>121</sup>Sb and <sup>123</sup>Sb can be determined from the measured relaxation curves using Eq. (3) and Eq. (4), respectively. In this paper we assume that the above-mentioned procedure is valid for arsenic as well, and extract  $W_m$  for <sup>75</sup>As using Eq. (2). In metals with substantial *s*-wave character, the magnetic contact interaction dominates the nucleus–carrier transition rate, and  $W_m$  depends on both the density of states at the Fermi surface [ $\rho(E_F)$ ] and the *s*-wave probability density at the nucleus ( $|u_k(0)|^2$ ) as follows:<sup>15</sup>

$$W_m \propto \rho^2(E_F) |u_k(0)|^4. \quad (5)$$

Calculations employing atomic wave functions and experimental Fermi surface parameters support the assumption that the contact interaction dominates nucleus–carrier interactions in the semimetals arsenic and antimony.<sup>10–12</sup>

### III. EXPERIMENTAL DETAILS

The pressure generation and measurement techniques have been described in detail elsewhere.<sup>5,16</sup> A piston-cylinder arrangement, designed to contain hydrostatic pressures of up to 3 GPa, with isopentane as the hydrostatic medium, was used. Pressure was measured to an accuracy of 2% by means of a manganin resistance manometer. All measurements were made at ambient temperature (295 K). The samples used were high purity (99.9999) annealed 20- $\mu$ m powders. Details of the sample preparation technique are given elsewhere.<sup>10,11</sup>

A coherent, pulsed NQR spectrometer, operating over the range 16–23 MHz, was used to make NSLR measurements using a standard three pulse inversion-recovery NQR spin-echo technique. The amplitude  $M(t)$  of the spin-echo generated by a  $\pi/2$ – $\pi$  sequence, at a time delay of  $t$  following an inversion pulse, is proportional to the difference in populations between the quadrupole energy levels. The relaxation curve  $(1 - M(t)/M_0)$  vs  $t$ , where  $M_0$  is the amplitude of the echo at thermal equilibrium, is then described by Eqs. (2)–(4). Measurements of the NSLR rates were made for the  $\frac{3}{2} \leftrightarrow \frac{1}{2}$  transition of <sup>75</sup>As in arsenic, the  $\frac{5}{2} \leftrightarrow \frac{3}{2}$  transition of <sup>121</sup>Sb in antimony, and the  $\frac{7}{2} \leftrightarrow \frac{5}{2}$  transition of <sup>123</sup>Sb in antimony. The pressure dependence of the NQR frequencies in arsenic and antimony have been discussed elsewhere.<sup>14</sup> The weak signals obtained in the high pressure cell necessitated

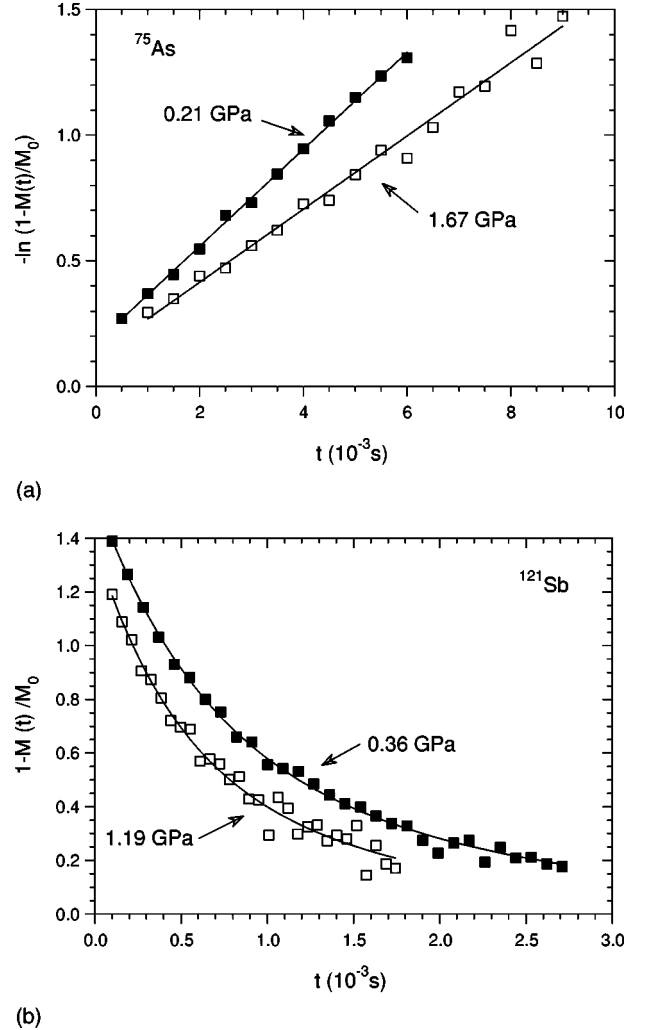


FIG. 1. (a) Single-exponential relaxation curves for <sup>75</sup>As in arsenic metal obtained at pressures of 0.21 and 1.67 GPa. (b) Double-exponential relaxation curves for <sup>121</sup>Sb in antimony metal obtained at pressures of 0.36 and 1.19 GPa. In both plots the data for the higher pressures show greater scatter due to the signal degradation mentioned in the text.

signal averaging of up to  $6.4 \times 10^3$  traces to maintain a signal-to-noise ratio of greater than 30:1.

The signal strength in both antimony and arsenic deteriorated under pressure. This effect limited the antimony measurements to a maximum of 1.4 GPa. The origin of this deterioration is not clear, but may be linked to skin depth effects becoming important at these pressures. No broadening of the NQR lines due to non-hydrostatic conditions was observed. The effect was, however, completely reversible.

### IV. RESULTS AND DISCUSSION

Relaxation curves for <sup>75</sup>As obtained at 0.21 and 1.67 GPa are shown in Fig. 1(a). Relaxation of <sup>75</sup>As is single exponential, and  $W_m$  is readily extracted from linear least squares fits of Eq. (2) to the linearized data. Relaxation is double exponential for <sup>121</sup>Sb and triple exponential for <sup>123</sup>Sb, and non-linear fitting techniques [Eqs. (3 and 4)] must be employed.

TABLE I. Magnetic nucleus–carrier transition rates for  $^{75}\text{As}$  in metallic arsenic,  $^{121}\text{Sb}$  in metallic antimony, and  $^{123}\text{Sb}$  in metallic antimony at 295 K and 1 atm.

	$W_m$ ( $\text{s}^{-1}$ )
$^{75}\text{As}$	$205 \pm 3$
$^{121}\text{Sb}$	$74.8 \pm 0.8$
$^{123}\text{Sb}$	$23.9 \pm 0.2$

Figure 1(b) shows representative relaxation curves of  $^{121}\text{Sb}$  in metallic antimony at 0.36 and 1.19 GPa. The transition rates  $W_m$  obtained at ambient pressure for all three isotopes are given in Table I.

The relaxation transition rates of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  were compared at three pressures: 0, 0.7, and 1.0 GPa. Values of the ratio  $R(P) = W_m^{121}/W_m^{123}$  at these pressures are given in Fig. 2. For purely magnetic relaxation, we expect  $W_m$  to be proportional to the square of the nuclear gyromagnetic ratio, and therefore expect an isotopic ratio of  $R = 3.41$ . The values of  $R$  obtained from the above-mentioned fitting procedures are approximately 10% lower than for purely magnetic relaxation, indicating the presence of observable quadrupolar effects. Our previous analysis of relaxation in antimony in terms of the full relaxation expressions<sup>9</sup> has shown, however, that since the coefficients of the quadrupolar transition rates in the relaxation expressions are much larger than those of the magnetic transition rates, this deviation in  $R$  corresponds to a very small quadrupolar contribution ( $< 2\%$ ). The  $W_m$  obtained from the magnetic fits were shown to be good measures of the magnetic transition probabilities.<sup>9</sup> The present measurements show that  $R$  does not change under pressure within experimental accuracy. This implies that the relative

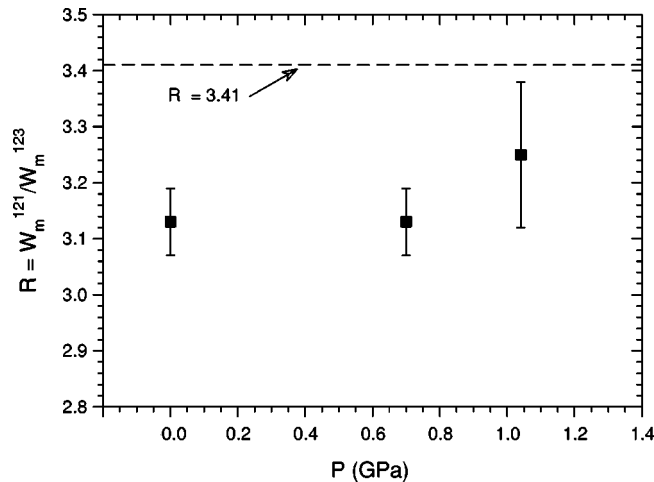


FIG. 2. Pressure dependence of the ratio of magnetic transition rates for  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ , obtained by assuming only magnetic relaxation. The deviation from  $(^{121}\gamma/^{123}\gamma)^2 = 3.41$  (dashed line) indicates the presence of small quadrupolar contributions to relaxation in antimony. It should be noted that we were unable to determine whether the quadrupolar contribution exhibited any pressure dependence, since the three measurements made are identical within experimental error.

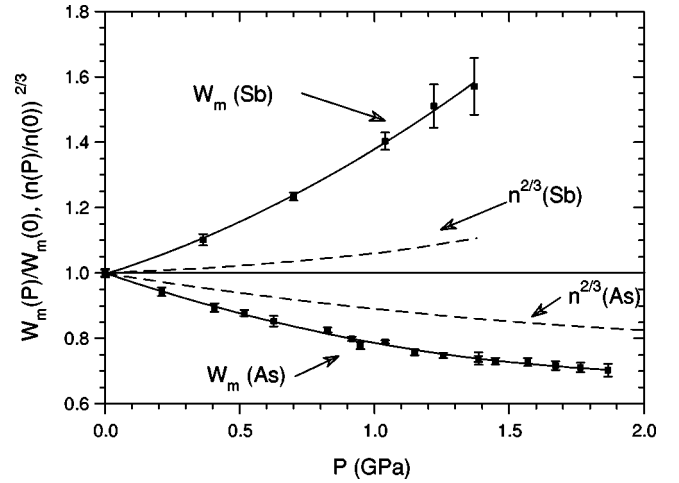


FIG. 3. Relative variation of the magnetic transition rate parameters in arsenic and antimony obtained in the present NQR measurements. The variation of the total carrier concentration obtained from previous transport measurements (dashed curves) is also shown.

quadrupolar relaxation rates in antimony do not change significantly under pressure. Unfortunately, a similar two-isotope analysis cannot be carried out in arsenic, for which only one isotope occurs. We will assume that quadrupolar relaxation rates are small at room temperature, and remain small under pressure, in arsenic as well.

Figure 3 shows the relative pressure variations of the magnetic transition rates of  $^{75}\text{As}$  in arsenic and  $^{121}\text{Sb}$  in antimony. The error bars shown are obtained from standard deviations of the least-squares fits. The behavior of the relaxation rate in antimony is strikingly different from that observed in arsenic. In antimony  $W_m$  increases by 56% in the 0- to 1.4-GPa range. This increase becomes more rapid with increasing pressure. For arsenic, on the other hand,  $W_m$  decreases under pressure, and flattens off at the highest pressures. A decrease of 29% is observed over the 0- to 2-GPa range in arsenic.

The magnetic relaxation rates are determined by the product  $\rho^2(E_F)|u_k(0)|^4$  [Eq. (5)]. We will assume for the moment that the carrier density at the nucleus does not have a strong pressure dependence, and analyze our results in terms of the density of states at the Fermi surface. The Fermi surface of arsenic and antimony consists of approximately ellipsoidal electron and hole pockets, which are well separated in  $k$ -space.<sup>1</sup> For an ellipsoidal Fermi surface we may write:

$$\rho(E_F) \propto v_0 n^{1/3} m^*, \quad (6)$$

where  $v_0$  is the atomic volume,  $n$  is the total carrier concentration, and  $m^* = (m_x m_y m_z)^{1/3}$  is an average effective mass parameter, written here in terms of the principal axes of the ellipsoid. Previous transport measurements of the pressure dependence of  $n$  at low temperature in arsenic<sup>3</sup> and antimony<sup>2</sup> are compared with our relaxation results in Fig. 3.  $n$  increases non-linearly in antimony, and decreases non-linearly in arsenic. The variation of  $n$  in arsenic, however, exhibits a minimum before increasing beyond 3 GPa.<sup>3</sup>

From the lattice parameter data,<sup>17,18</sup> we infer that the atomic volume decreases by 5% at 2 GPa in arsenic, and by 3.5% at 1.4 GPa in antimony. Equation (6), together with the experimental data for  $W_m$  and  $n$ , therefore implies a fairly strong increase in the average carrier effective masses in antimony, and a somewhat weaker decrease in  $m^*$  in arsenic. This result is consistent with available oscillatory data in antimony.<sup>4</sup>

The different pressure effects on the ES of arsenic and antimony are apparent in the pseudopotential calculations of Pospelov.<sup>6,7</sup> Pospelov obtains a minimum in the band overlap in arsenic between 2 and 4 GPa, while the band overlap in antimony increases monotonically with pressure. Pospelov attributes the non-monotonic variation in the band overlap in arsenic to the anomalous pressure dependence of the nearest-neighbor distance  $R_1$ . In arsenic  $R_1$  increases initially under pressure due to a rapid increase in the rhombohedral angle  $\alpha$ . Beyond approximately 3 GPa, the increase in  $\alpha$  slows and  $R_1$  decreases.<sup>19</sup> In antimony  $R_1$  decreases monotonically with pressure. The previously mentioned transport measurements<sup>2,3</sup> are consistent with Pospelov's calculations.

Preliminary FLAPW calculations indicate that the density of states at the Fermi surface increases with pressure in antimony, and decreases with pressure in arsenic<sup>20</sup> in the 0- to 2-GPa range, in qualitative agreement with our relaxation data. The relaxation rates  $W_m$  measured in this paper would

also be sensitive to changes in the carrier wave functions. This includes the  $s$ -wave density at the nucleus, and the fractional  $s$ -wave character of the carriers. These relaxation data therefore provide a critical test for modern electronic structure calculation techniques.

## V. CONCLUSION

Nuclear spin-lattice relaxation in pure arsenic and antimony metal has been investigated at 295 K up to 2.0 and 1.4 GPa, respectively, using pulsed NQR. Previous experiments in antimony show that the relaxation rate parameters obtained in these measurements are determined by magnetic nucleus-carrier interactions.<sup>9</sup> Our results indicate that antimony becomes more metallic under pressure, while arsenic becomes less metallic, which is qualitatively consistent with previous experimental and theoretical investigations. In addition to Fermi surface parameters, the magnetic relaxation rates measured in this paper depend on the fractional  $s$ -wave character of the carriers and the  $s$ -wave carrier density at the nucleus. A previous *ab initio* calculation of detailed electronic properties in all three Group V semimetals at ambient pressure<sup>21</sup> has provided results in excellent agreement with experiment. The data presented in this paper should provide a useful comparison with detailed calculations at high pressures.

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