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Abstract
The nuclear calibration constant α for ^{121}Sb is calculated from the correlation between the experimental isomer shift (IS) and theoretical contact charge densities. The contact charge densities are calculated using the full-potential linear augmented-plane-wave method, within both the local density and the generalized gradient approximations. The IS for Sb in various phases of InSb under pressure is then calculated. This study shows that before the transition of InSb to a metallic state, the Sb IS becomes more positive with increasing pressure. After each subsequent phase transformation the IS shows a large change in the negative direction. These results used in conjunction with Mössbauer experiments may be useful in identifying phases of InSb at high pressure.

1. Introduction

The III–V zinc-blende compounds are interesting materials with important applications in electronic devices. These compounds are semiconducting at ambient pressure and become metallic under high pressures. Indium antimonide has a zinc-blende (P1) structure at ambient conditions and metallizes along with undergoing a structural transition around 2 GPa. The structures of the new phase and subsequent pressure-stabilized phases have been the subject of extensive and conflicting studies over the past four decades [1–7]. One of the more recent and thorough investigations up to 5 GPa was by Nelmes *et al* [8, 9]. They discovered two distinct pathways corresponding to either a rapid or a gradual increase in pressure, namely

$$P1 \longrightarrow P(2+3) \longrightarrow P3 \longrightarrow P4 \tag{1}$$

$$P1 \longrightarrow P4, \tag{2}$$

where P1 is the cubic zinc-blende phase, P2 is the tetragonal diatomic analogue of β-tin, P3 is an orthorhombic distortion of P2 and P4 is an orthorhombic superstructure with average space group $Pmm2$. Vanderborgh *et al* [7] have studied InSb up to 66 GPa. Above 6 GPa they found a new phase (PV) which continuously transformed to hexagonal PIII at 17.5 GPa. There was a

further transformation at 28 GPa either to an ordered CsCl-type (PVI) structure (space group $Pm\bar{3}m$) or to a disordered bcc structure. This complexity of the phase diagram of InSb as well as the inherent difficulties in performing x-ray diffraction experiments at elevated pressures has motivated us to calculate the Mössbauer isomer shift (IS) for ^{121}Sb in most of the observed phases. Our calculated ISs may serve as references for future high-pressure work on InSb.

The IS is a function of the so-called contact charge density [10] which can be obtained from theoretical calculations. In its simplest form the contact charge density is defined as the electronic charge density at the site of the nuclear position. The relation between the contact charge density of the Mössbauer absorber, $\rho_a(0)$, the source, $\rho_s(0)$, and the IS is [11]

$$S = \alpha[\rho_a(0) - \rho_s(0)].$$

The contribution to $\rho(0)$ comes from the core electron density, $\rho_c(0)$, as well as from the valence charge density, $\rho_v(0)$. The nuclear parameter α is proportional to the change in mean square radius between the ground state and the excited state of the particular Mössbauer nucleus. $\alpha = \beta\Delta\langle r\rangle^2$ where β is a numerical constant for a given isotope (for ^{121}Sb $\beta = 8.4\,a_0^3$ mm s^{-1} fm^{-2} with a_0 being the Bohr radius [12]). The compound used as the source in the majority of ^{121}Sb Mössbauer experiments is BaSnO$_3$. By comparing the experimental IS and calculated contact charge densities for a series of compounds [10,13–15] we can determine α. Once the value of α is known we can calculate the IS of any ^{121}Sb compound from its contact charge density. This calibration constant has been calculated previously. Lippens [15] have used the tight-binding method and found $\alpha = -0.294\,a_0^3$ mm s^{-1}. Svane and Antoncik [16] used the linear-muffin-tin-orbital method with the atomic sphere approximation (ASA) and obtained $\alpha = -0.369\,a_0^3$ mm s^{-1}. Ruby *et al* [17] used the Hartree–Fock method and obtained $\alpha = -0.302\,a_0^3$ mm s^{-1}. In all of the above the value of α is calculated by comparison between the experimental IS and the calculated valence charge density.

In the present work we also calculate the value of α by comparing our calculated total contact charge density (i.e. including the core charge density) to the experimental isomer shifts of various Sb compounds. This value of α is further used to calculate the Mössbauer IS of the Sb nuclei in the high-pressure phases of InSb. In doing this we highlight the effect of pressure on the electronic charge density.

2. Methodology

Total-energy calculations are performed using the full-potential linear augmented-plane-wave (FP-LAPW) method using the WIEN97 code [18]. The high-lying Sb 4d states are treated using local orbitals. Scalar relativistic equations are used in a self-consistent scheme. The calculations are performed using the local density approximation (LDA). Also, the effect of replacing the LDA with the generalized gradient approximation (GGA) for the exchange–correlation potential has been studied. In the present work we use the GGA derived by Perdew and Wang [19].

The contact charge density of the Sb nucleus is calculated by modelling the nucleus as a uniformly charged sphere of radius $R = 1.2A^{1/3}$ fm [31], where the mass number A for the Sb Mössbauer nuclei is $A = 121$. The contact charge density is thus an average of the electronic charge density over the nuclear volume.

All the calculations are converged in terms of basis functions as well as in the size of the k-point mesh representing the Brillouin zone.

The lattice parameters of the different high-pressure phases of InSb along with the experimental pressures at which they exist are given in table 1. We have omitted InSb PV as no structural determination has been performed.
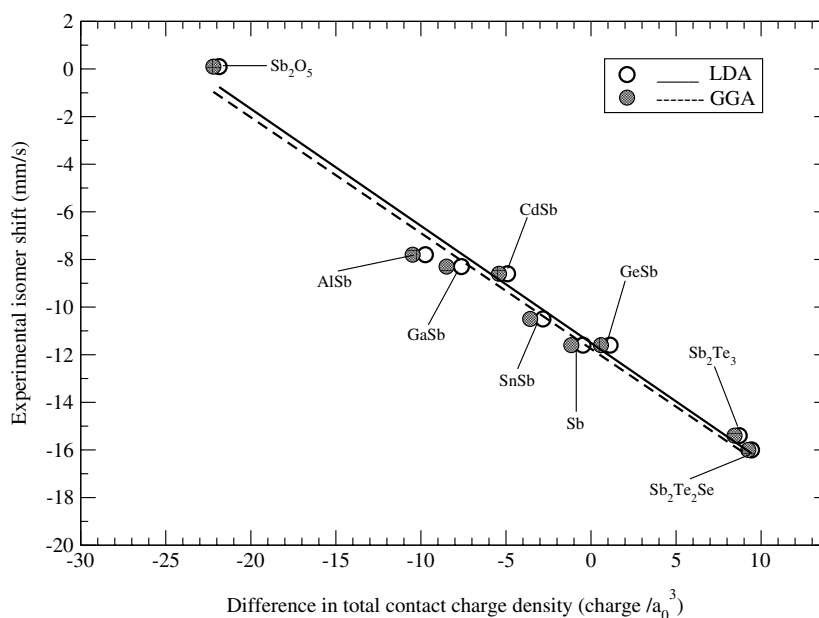
Figure 1. Experimental ISs versus the difference in total contact charge density between the absorber and the source.

Table 1. Lattice parameters and space groups of various phases of InSb under high pressure at room temperature.

Phase (pressure GPa)	Space group	Lattice parameter (Å)			Reference
		a	b	c	
P1 (0.0)	$F\bar{4}3m$	6.480	6.480	6.480	[20]
P1 (0.6)	$F\bar{4}3m$	6.450	6.450	6.450	[20]
P1 (1.6)	$F\bar{4}3m$	6.400	6.400	6.400	[20]
P1 (3.0)	$F\bar{4}3m$	6.360	6.360	6.360	[20]
P2 (2.1)	$I\bar{4}m2$	5.697	5.697	3.104	[8]
P3 (2.3)	$Imm2$	5.847	5.388	3.181	[8]
P4 (3.0)	$Pmm2$	2.925	5.617	3.067	[8]
PIII (17.5)	$Pmmm$	5.720	5.357	3.063	[21]
PVI (28.0)	$Pm\bar{3}m$	3.390	3.390	3.390	[7]

3. Results and discussion

In figure 1 we plot several experimental ISs (values taken from [22] and [15] and references therein) against the difference in total contact charge density between the absorber and the source obtained from calculations performed within the LDA as well as the GGA. Like in the experiments, $BaSnO_3$ is used as the source material for all the calculations. The best linear fit of the contact charge densities calculated within LDA to the experimental ISs gives the value of $\alpha = -0.491 \pm 0.02\, a_0^3\, mm\, s^{-1}$. Replacing the LDA with the GGA does not change the value of α significantly. The linear fit of the contact charge densities calculated using the GGA against the experimental isomer shifts gives the value of α as $-0.486 \pm 0.02\, a_0^3\, mm\, s^{-1}$. These values of α are in general agreement with the experimental measurements but are slightly higher than
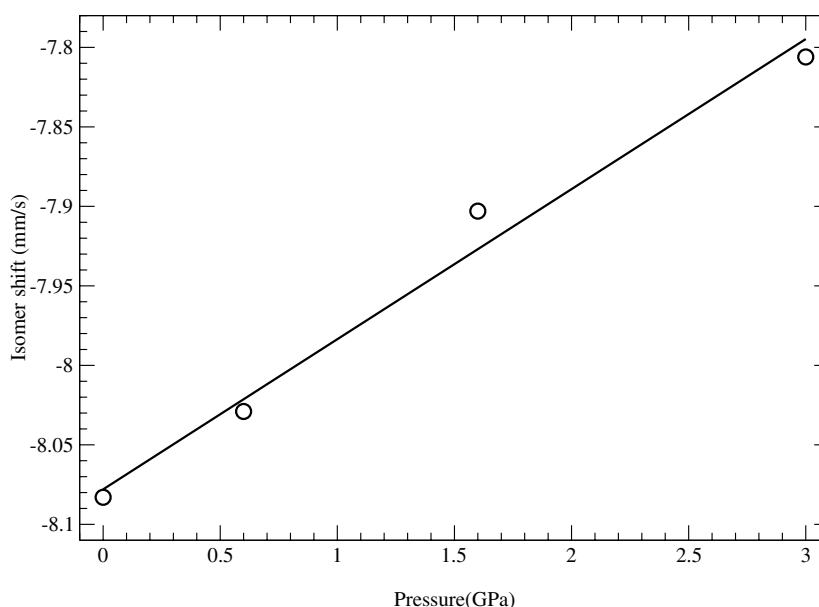
Figure 2. The pressure dependence of the Sb IS in InSb (P1 phase).

the earlier calculated values [15–17,23]. There could be two reasons for this disagreement with the previous calculations. The first is the inclusion of the core electronic charge density and the second is that we have not made any shape approximation for the potential (calculations have been performed using state-of-the-art FP-LAPW method) and thus our results are more reliable compared to those from the tight-binding method or ASA used earlier [15, 16].

It has been observed from high-pressure measurements of the Mössbauer IS in metallic Fe, Ta and Au [24–26] that the total contact charge density increases with increasing pressure. This is in contrast to the behaviour found for β-Sn [27] and metallic Sb [27, 28] which showed a decrease in the contact charge density with increasing pressure. Our calculated values of the pressure-dependent ISs of Sb nuclei in the InSb compound in the P1 phase are shown in figure 2. As with previous calculations for β-Sn and metallic Sb [28, 29], we use the linear relation

$$S(P) = S_0 + P \frac{\mathrm{d}S}{\mathrm{d}P}$$

$S_0 = -8.077$ mm s^{-1} and $\mathrm{d}S/\mathrm{d}P = +0.094$ mm s^{-1} GPa^{-1}. Metallic Sb ($\mathrm{d}S/\mathrm{d}P = 0.03$ mm s^{-1} GPa^{-1}) shows similar behaviour, but the value of $\mathrm{d}S/\mathrm{d}P$ is larger for Sb in InSb.

More interestingly, the IS of InSb shows a sudden and large decrease upon metallization (table 2). Further discontinuous decreases in the IS are seen for the transformations P2 $\rightarrow$ P3 $\rightarrow$ P4 $\rightarrow$ PIII $\rightarrow$ PVI though the magnitude of the change is smaller. The valence contact charge densities (in units of charge/a_0^3) and the ISs of the Sb nuclei for different phases of InSb are presented in table 2. It may be noted that it is easy to distinguish between the P2, P3, P4 and PIII phases using the value of the Sb IS.

Following Flinn [30] we also fit our calculated IS to a non-linear function of the occupation numbers for the s and p valence electrons of the Sb atom. In our calculations we use the number of valence electrons having s and p character integrated over the non-overlapping muffin-tin

Table 2. The valence contact charge density, N_s and N_p for Sb nuclei in various phases of InSb under pressure. The muffin-tin radius for Sb atoms is 2.0 a_0.

Phase	N_s	N_p	$\rho_v(0)$	IS (mm s^{-1})
P1(0.0)	0.791	0.757	97.31	−8.08
P1(0.6)	0.790	0.763	97.07	−8.03
P1(1.6)	0.788	0.772	96.79	−7.90
P1(3.0)	0.786	0.779	96.57	−7.81
P2	0.832	0.686	103.50	−10.88
P3	0.837	0.686	104.19	−11.19
P4	0.847	0.672	105.60	−11.81
PIII	0.863	0.645	106.87	−12.37
PVI	0.877	0.640	106.98	−12.42

sphere as the occupation number. A large proportion of the valence electrons will leak out into the interstitial region and so we will only count a certain fraction of the s and p electrons. Our occupation numbers depend on the muffin-tin radius (R_{MT}), which is kept constant for Sb atoms in the different phases of InSb. If N_s and N_p are the fractional occupation numbers of the s and p valence orbitals respectively, then the IS may be fitted with

$$S = -58.1N_s + 5.37N_s^2 + 13.51N_sN_p + 25.89 \text{ mm s}^{-1}.$$

The strong linear behaviour in N_s indicates that each phase transition results in a gain of s-type electrons in the valence band. However, before metallization, when InSb is still in the P1 phase, increase in pressure causes a loss of the s electrons and therefore the IS becomes more positive. The other thing that can be noticed is that $N_s + N_p$ remains almost constant for Sb sites in various phases of InSb (table 2 shows the values of N_s and N_p for all of the phases of InSb with $R_{MT} = 2.0\ a_0$ for the Sb atom). In order to study the effect of the muffin-tin radius on $N_s + N_p$ the calculations are performed for five different values of the muffin-tin radii for the Sb atoms in all the phases of InSb ($R_{MT} = 2.0, 2.2, 2.3, 2.5, 3.0\ a_0$). It was found that $N_s + N_p$ remains constant and increases equally for all the phases with increase in R_{MT} ($N_s + N_p \sim 1.52, 2.03, 2.30, 2.80, 3.20$ for $R_{MT} = 2.0, 2.2, 2.3, 2.5, 3.0\ a_0$ respectively in all the phases of InSb).

4. Summary

The contact charge densities for various Sb compounds have been calculated using the FP-LAPW method within the LDA as well as the GGA. By comparing these data with the experimental isomer shifts, the nuclear parameter α for ^{121}Sb is determined. The change in the value of α on replacing the LDA with the GGA is found to be insignificant. Our calculated value of α is in good agreement with the experimental measurements but slightly higher than the earlier calculated values. There could be two reasons for this disagreement with the previous calculations. The first is the inclusion of the core electronic charge density and the second is that we have not made any shape approximation for the potential and thus our results are more reliable compared to those from the tight-binding method or ASA used earlier [15, 16].

Using the value for α we determined the pressure and phase dependence of the IS of Sb in InSb. In the low-pressure regime for the P1 phase of InSb the Sb IS has a large positive pressure dependence ($\mathrm{d}S/\mathrm{d}P = +0.094$ mm s^{-1} GPa^{-1}). The initial increase in IS with pressure is due to decrease in the number of s electrons and an increase in the number of p electrons. After

each phase transition the number of s electrons increases discontinuously (and p decreases) causing the IS to become more negative. It was also found that $N_s + N_p$ for the Sb nuclei in InSb is constant for the different phases and increases equally for all the phases on increasing the muffin-tin radius. We expect that, with our calculated IS results, the high-pressure phases of InSb will be easier to identify.

Acknowledgments

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