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Antimony-121 Mössbauer Spectral Study of  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub>

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The Mössbauer spectra of  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub>, a compound that is best formulated as  $\alpha$ -Zn<sub>13</sub>Sb<sub>10</sub> or  $(\text{Zn}^{2+})_{13}(\text{Sb}^{3-})_6(\text{Sb}_2^{4-})_2$ , have been measured between 5 and 120 K. The resulting six spectra have been simultaneously fit with two components in the ratio of 3:2 corresponding to the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions identified in this valence semiconductor. The fits yield temperature independent isomer shifts of  $-8.17(2)$  and  $-9.73(2)$  mm/s and quadrupole interactions of  $-4.9(2)$  and  $0$  mm/s for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions, respectively; the corresponding Mössbauer temperatures are 197(5) and 207(5) K, temperatures that are lower than the Debye temperature of  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub>. The isomer shifts correspond to electronic configurations between  $5s^25p^6$  and  $5s^{1.75}5p^{4.01}$  for the  $\text{Sb}^{3-}$  ions and between  $5s^25p^5$  and  $5s^{1.80}5p^{3.38}$  for the  $\text{Sb}^{2-}$  ions, configurations that are in good agreement with the expected configurations for this valence semiconductor and with the results of band structure calculations.

## Introduction

The semiconducting compound  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> is a thermoelectric material with a high figure of merit; its structure and properties have been reviewed by Snyder et al.<sup>1</sup> and Mozharivskiy et al.<sup>2,3</sup>  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> has two crystallographically distinct antimony sites, the 18e site which contains  $\text{Sb}^{3-}$  and the 12c site which contains  $\text{Sb}^{2-}$ . The 12c sites form dumbbell shaped  $\text{Sb}_2^{4-}$  dimers. Below approximately 260 K, rhombohedral  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> undergoes a reversible phase

transition to triclinic<sup>4</sup>  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub>. The ideal valence balanced stoichiometry<sup>3,4</sup> of Zn<sub>4</sub>Sb<sub>3</sub> is actually Zn<sub>13</sub>Sb<sub>10</sub>. Although in  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub> the crystallographic degeneracies of the 18e and 12c sites are lowered and there are 20 unique  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  sites, the low temperature  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub> phase may still be formulated<sup>4</sup> as  $(\text{Zn}^{2+})_{13}(\text{Sb}^{3-})_6(\text{Sb}_2^{4-})_2$ , and the ratio of the  $\text{Sb}^{3-}$  to  $\text{Sb}^{2-}$  sites remains 3:2 in both phases.

The exceptionally low thermal conductivity of  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> has been ascribed<sup>1</sup> to the high degree of intricate disorder in the zinc portion of this compound. In contrast, the  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub> phase<sup>4</sup> is a completely ordered phase. The complete understanding and the improvement of the thermoelectric properties resulting from the complex disorder found in  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> will require an in-depth description of the electronic

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configurations and the dynamic properties of the zinc and antimony in both the  $\alpha$ - $\text{Zn}_4\text{Sb}_3$  and the  $\beta$ - $\text{Zn}_4\text{Sb}_3$  phases.

Antimony-121 Mössbauer spectroscopy is an ideal technique<sup>5–7</sup> to selectively probe both the electronic configuration of antimony through its isomer shift and the quadrupole interaction and its dynamic properties through its Mössbauer temperature. Herein, we report and analyze the antimony-121 Mössbauer spectra obtained for the ordered  $\alpha$ - $\text{Zn}_4\text{Sb}_3$  phase, a phase that must be characterized with as much accuracy as possible before the highly disordered  $\beta$ - $\text{Zn}_4\text{Sb}_3$  phase can be successfully investigated in detail with the goal of improving its thermoelectric properties.

## Experimental Section

$\text{Zn}_{3.97}\text{Sb}_3$  was prepared by the same direct reaction of the elements as was used in a previous study.<sup>8</sup> The  $\text{Zn}_{3.97}\text{Sb}_3$  stoichiometry is in the middle of the experimental stability range for  $\text{Zn}_4\text{Sb}_3$  and was chosen to ensure that the material was single-phase.

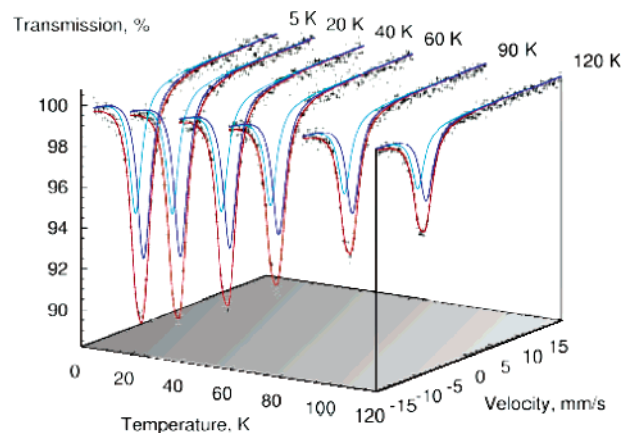
The Mössbauer spectra were obtained with a conventional constant acceleration spectrometer which utilized a room-temperature source with approximately 0.2 mCi of tin-121\* in  $\text{CaSnO}_3$  and was calibrated at room temperature with  $\alpha$ -iron foil and InSb. The absorber was mounted in the vacuum space of a Janis liquid helium cryostat and its temperature was controlled by a commercial sensor and heater.

Because of the difficulty in obtaining good antimony-121 Mössbauer spectra, especially at higher temperatures, the  $\alpha$ - $\text{Zn}_4\text{Sb}_3$  Mössbauer spectral absorber thickness, which is 32 mg/cm<sup>2</sup> of sample, 18.7 mg/cm<sup>2</sup> of natural abundance antimony, or 10.7 mg/cm<sup>2</sup> of antimony-121, has been selected to maximize the resonant absorption and to minimize the non-resonant scattering and, thus, to maximize the spectral signal-to-noise ratio.<sup>9</sup> By assuming a Mössbauer temperature of 200 K (see below) this absorber thickness corresponds to an optical thickness for the antimony-121 spectral absorption of 6.1, 2.6, and 0.72 at 5, 120, and 240 K, respectively. These values indicate that the absorber is rather thick, especially at the lower temperatures, and have necessitated the inclusion of a thickness broadening correction in the spectral analysis discussed below. Further, because the antimony-121 recoil free fraction decreases rapidly with increasing temperature, it has proven difficult, if not impossible, to obtain useful spectra above 120 K with a room-temperature source.

All isomer shifts are given relative to the  $\text{CaSnO}_3$  source, values which are identical to those given relative to  $\text{BaSnO}_3$ .

## Results and Discussion

The antimony-121 Mössbauer spectra of  $\alpha$ - $\text{Zn}_4\text{Sb}_3$  obtained between 5 and 120 K are shown in Figure 1. All of the spectra exhibit a broad absorption that can first be fit with a single quadrupole broadened component and a



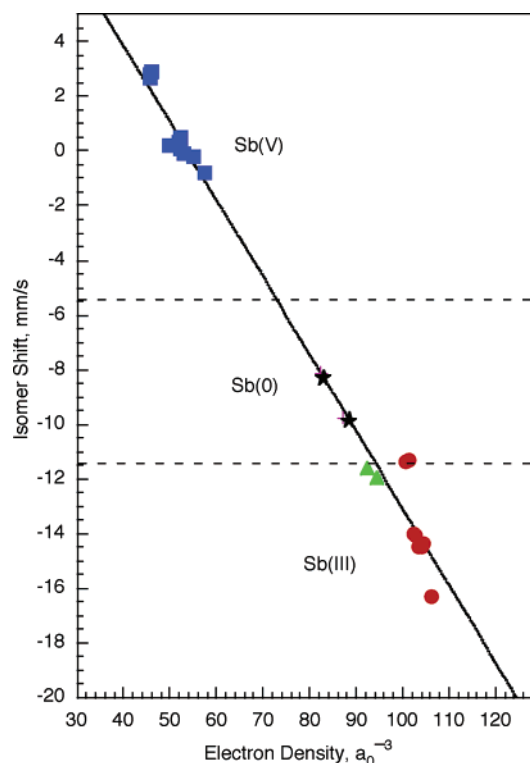
**Figure 1.** Mössbauer spectra of  $\alpha$ - $\text{Zn}_4\text{Sb}_3$  obtained between 5 and 120 K.  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$  spectral components are represented by the dark blue and cyan lines, respectively.

Mössbauer temperature of 197 K. Because, in this valence semiconductor, antimony is expected<sup>1–4</sup> to be present as  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$ , a more physically meaningful fit with two components has been carried out, a fit that represents the best resolution-limited model for the 20 antimony crystallographic sites<sup>3</sup> occupied by  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$  ions in a 3:2 ratio. Unfortunately, as is shown by the spectra in Figure 1, antimony-121 Mössbauer spectroscopy is not capable of resolving several antimony sites with different valences because of its intrinsic broad natural line width of 2.10(12) mm/s. Hence, any fits must be restricted to, at most, two types of sites, in this case the  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$  sites.

A three-dimensional array of the temperature, velocity, and percent transmission of the spectra has been simultaneously fit with a complete model that is based on the structural and physical properties of the material. First, on the basis of the structural work,<sup>3,4</sup>  $\alpha$ - $\text{Zn}_4\text{Sb}_3$  has antimony in two different formal oxidation states, namely,  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$ , states whose occupancies are in a 3:2 ratio. Second, the  $\text{Sb}^{2-}$  ions are expected to have a small or zero quadrupole interaction because of their close to threefold point symmetry. Third, the spectral components resulting from the  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$  ions do not necessarily have the same Mössbauer temperature. Preliminary fits indicated that the isomer shifts are essentially temperature independent. Finally, the quadrupole interaction of the  $\text{Sb}^{3+}$  component was assumed to be temperature independent. Hence, the model uses a total of seven physical parameters and one parameter for each temperature, namely, the baseline. These parameters are the isomer shift and the Mössbauer temperature for the  $\text{Sb}^{3+}$  and  $\text{Sb}^{2-}$  sites, the quadrupole interaction for the  $\text{Sb}^{3+}$  site, a common line width for both sites, a total area parameter corresponding to the total area at “0 K”, and the baseline for each temperature. The six fits have a reduced  $\chi^2$  smaller than 1.03 and, hence, are excellent, as is shown in Figure 1.

In general, one would expect the isomer shift to be somewhat dependent on temperature because of the second-order Doppler shift, a shift that occurs when the source and absorber are at different temperatures as is the case herein. Thus, the spectra have also been fit with a model in which

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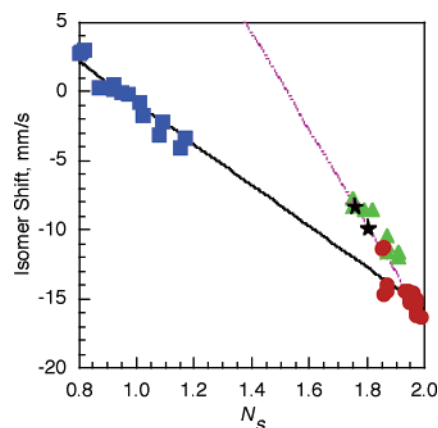


**Figure 2.** Correlation between the experimental values of the antimony-121 Mössbauer effect isomer shift, relative to CaSnO<sub>3</sub>, and the calculated values of the electron density at the nucleus for the Sb(V), squares, Sb(0), triangles and pluses, and Sb(III), circles, compounds. The data is taken from refs 11 and 12. The stars correspond to  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub>.

the isomer shift is permitted to vary within the second-order Doppler shift model<sup>10</sup> with the observed Mössbauer temperature (see below). The resulting fits are equally as good as the fits shown in Figure 1, and they reveal that the maximum variation in the isomer shift is very small at +0.02 mm/s and equal to the statistical error on the isomer shift between 5 and 120 K. Other models for the temperature dependence lead to even smaller variations in the isomer shift. Thus, this very small variation validates the above assumption of a temperature independent isomer shift.

Because of the possibility of thickness broadening of the  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub> spectra at lower temperatures, an additional fit was undertaken in which a linear increase in the spectral line width upon cooling was assumed. The results, which are virtually identical to those shown in Figure 1, indicated that the line width increased by at most 0.45 mm/s upon cooling from 120 to 5 K; the resulting hyperfine parameters were the same within experimental error. Further, the increase in line width upon cooling is approximately the same as that observed<sup>7</sup> for InSb spectra when the differences in absorber thickness are considered. The observed misfit values indicate that there is little statistical difference between the two types of fits.

Mössbauer temperatures of 197(5) and 207(5) K and isomer shifts of -8.17(2) and -9.73(2) mm/s relative to



**Figure 3.** Correlation between the experimental values of the antimony-121 Mössbauer effect isomer shift, relative to CaSnO<sub>3</sub>, and the calculated number of antimony 5s electrons,  $N_s$ , for the Sb(V), squares, Sb(0), triangles, and Sb(III), circles, compounds. The solid line represents a fit to the Sb(V) and Sb(III) data whereas the dotted line represents a fit to the Sb(0) and Sb(III) data points. The data is from refs 11 and 12. The stars correspond to  $\alpha$ -Zn<sub>4</sub>Sb<sub>3</sub>.

CaSnO<sub>3</sub> were obtained for the Sb<sup>3-</sup> and Sb<sup>2-</sup> sites, respectively. A quadrupole interaction of -4.9(2) mm/s was obtained for the Sb<sup>3-</sup> sites. A release of the constrained zero quadrupole interaction for the Sb<sup>2-</sup> sites leads to a very small value for this quadrupole interaction. A relaxation of the 3:2 occupancy constraint leads, at most, to small changes in this ratio.

The fitted common line width of 2.82(5) mm/s is only slightly larger than the line width of 2.73(3) mm/s observed<sup>7</sup> in InSb at 90 K and, no doubt, reflects the existence of several crystallographic sites for both the Sb<sup>3-</sup> and the Sb<sup>2-</sup> contributions.

The isomer shifts observed for the two components occur in the range of the isomer shifts observed<sup>11,12</sup> for the Sb(0) valence state in antimony semiconducting compounds such as InSb, as is illustrated in Figure 2. From the linear correlation in this figure, electron densities at the antimony nucleus of 82.6 and 88.1 electrons/ $a_0^{-3}$ , where  $a_0$  is the Bohr radius, are obtained for Sb<sup>3-</sup> and Sb<sup>2-</sup> ions, respectively. The formal electronic configurations of the Sb<sup>3-</sup> and Sb<sup>2-</sup> ions are 5s<sup>2</sup>5p<sup>6</sup> and 5s<sup>2</sup>5p<sup>5</sup> and differ only by the number of 5p electrons, 5p electrons that, when compared to the 5s electrons, have a reduced screening influence on the s-electron density at the antimony nucleus and hence on the observed isomer shifts. This reduced influence is illustrated in Figure 3 which shows, as a solid line, the dominant influence of the 5s electrons on the isomer shifts in a series<sup>7,11</sup> of Sb(V) and Sb(III) compounds and, as a dotted line, the secondary screening effect of the 5p electrons in a series<sup>7,11,12</sup> of Sb(0) and Sb(III) compounds. The combined influence of the  $N_s$  and  $N_p$  number of 5s and 5p electrons on the electron density at the antimony nucleus,  $\rho(0)$ , has been formulated<sup>4</sup> as

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$$\rho(0) = 0.11 + 68.65N_s - 3.39N_p - 5.57N_s^2 - 1.00N_sN_p \quad (1)$$

From the above determined electron densities at the antimony nucleus and with the assumption that the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions in  $\alpha\text{-Zn}_4\text{Sb}_3$  have two 5s electrons, eq 1 yields  $N_p$  values of 6.00 and 5.00 for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions. Hence, the electronic configurations of the two antimony ions determined from the observed isomer shifts would be  $5s^25p^6$  and  $5s^25p^5$ , in perfect agreement with the expected<sup>4</sup> electronic configurations for the valence semiconductor description of  $\alpha\text{-Zn}_4\text{Sb}_3$  or  $\text{Zn}_{13}\text{Sb}_{10}$ .

An alternate treatment of the observed isomer shifts and of Figures 2 and 3 can also be used. From Figure 3, a number of 5s electrons,  $N_s$ , equal to 1.75 and 1.80 for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  sites can be introduced into eq 1. This yields 4.01 and 3.38 for the number of 5p electrons,  $N_p$ , for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions, respectively. These values correspond to electronic configurations of  $5s^{1.75}5p^{4.01}$  and  $5s^{1.80}5p^{3.38}$  for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions, respectively. These two sets of electronic configurations constitute limiting values for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions and can be compared with the results<sup>3</sup> of electronic structure calculations in  $\beta\text{-Zn}_{13}\text{Sb}_{10}$ . These calculations indicate that the 5s states of both the  $\text{Sb}^{3-}$  and the  $\text{Sb}^{2-}$  ions are fully occupied at approximately  $-11$  eV below the Fermi level and that the 5p states of both the  $\text{Sb}^{3-}$  and the  $\text{Sb}^{2-}$  ions contribute to the valence band between  $-7.7$  and  $-1.7$  eV below the Fermi level. Hence, the electronic configurations of  $5s^25p^6$  and  $5s^25p^5$  are in full agreement with these calculations and support the view that  $\alpha\text{-Zn}_4\text{Sb}_3$  or  $\text{Zn}_{13}\text{Sb}_{10}$  is an intrinsic valence semiconductor, with an essentially ionic formula,  $(\text{Zn}^{2+})_{13}(\text{Sb}^{3-})_6(\text{Sb}^{2-})_4$ , as predicted<sup>13</sup> by the Zintl formalism.

The temperature dependence of the Mössbauer spectral absorption area provides information about the lattice properties of a compound.<sup>7,14–16</sup> This temperature dependence, which is very apparent in Figure 1, has been fit with the

Debye model for the recoil-free fraction.<sup>14</sup> Two Mössbauer temperatures,  $\Theta_M$ , of 197(5) and 207(5) K have been obtained for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions, respectively. The Mössbauer temperature may be compared with the Debye temperature, an important parameter for determining the viability of potential thermoelectric materials. A Debye temperature of 237 K has been obtained<sup>17</sup> for  $\beta\text{-Zn}_4\text{Sb}_3$  from mean sound velocity measurements. The two Mössbauer temperatures measured herein are somewhat smaller than this Debye temperature and may indicate the presence of a soft vibrational mode associated with the antimony anions, perhaps the  $\text{Sb}^{2-}$  dimers. The observed values for  $\alpha\text{-Zn}_4\text{Sb}_3$  are, however, very typical of intermetallic compounds. A Mössbauer temperature of 201(1) K was found<sup>6</sup> in  $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$ , and values<sup>7,18</sup> of 175(4) and 160(5) K were found for  $\text{InSb}$ . In contrast, the Mössbauer temperatures obtained herein are somewhat larger than the values of 165 to 180 K obtained<sup>17</sup> for antimony metal but are similar to the Debye temperatures of 204 to 211 K determined<sup>19</sup> macroscopically for antimony metal.

Even though it is often not easy to distinguish, by antimony-121 Mössbauer spectroscopy because of the inherent line width of the antimony-121 transition, different antimony sites or valence states in a compound, we have been able to separate the contributions of the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions and to propose their limiting electronic configurations by using a simultaneous fit of a series of antimony-121 Mössbauer spectra of  $\alpha\text{-Zn}_4\text{Sb}_3$  at different temperatures. The  $5s^25p^6$  and  $5s^25p^5$  electronic configurations for the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  ions, respectively, are in excellent agreement with band structure calculations<sup>3</sup> and the Zintl formalism<sup>13</sup> applied to this valence semiconductor. Furthermore, this simultaneous fit provides the Mössbauer lattice temperatures of the  $\text{Sb}^{3-}$  and  $\text{Sb}^{2-}$  contributions, temperatures that are smaller than the Debye temperature of  $\beta\text{-Zn}_4\text{Sb}_3$ . We believe that this detailed description of the ordered  $\alpha\text{-Zn}_4\text{Sb}_3$  will help us develop a better understanding of  $\beta\text{-Zn}_4\text{Sb}_3$  and, hence, improve its thermoelectric properties.

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