

Antimony-121 Mössbauer Spectral Study of α -Zn₄Sb₃

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The Mössbauer spectra of α -Zn₄Sb₃, a compound that is best formulated as α -Zn₁₃Sb₁₀ 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 Sb^{3-} and 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 Sb^{3-} and Sb^{2-} ions, respectively; the corresponding Mössbauer temperatures are 197(5) and 207(5) K, temperatures that are lower than the Debye temperature of β -Zn₄Sb₃. The isomer shifts correspond to electronic configurations between $5s^25p^6$ and $5s^{1.75}5p^{4.01}$ for the Sb^{3-} ions and between $5s^25p^5$ and $5s^{1.80}5p^{3.38}$ for the 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 β -Zn₄Sb₃ is a thermoelectric material with a high figure of merit; its structure and properties have been reviewed by Snyder et al.¹ and Mozharivskiy et al.^{2,3} β -Zn₄Sb₃ has two crystallographically distinct antimony sites, the 18e site which contains Sb^{3-} and the 12c site which contains Sb^{2-} . The 12c sites form dumbbell shaped Sb_2^{4-} dimers. Below approximately 260 K, rhombohedral β -Zn₄Sb₃ undergoes a reversible phase

transition to triclinic⁴ α -Zn₄Sb₃. The ideal valence balanced stoichiometry^{3,4} of Zn₄Sb₃ is actually Zn₁₃Sb₁₀. Although in α -Zn₄Sb₃ the crystallographic degeneracies of the 18e and 12c sites are lowered and there are 20 unique Sb^{3-} and Sb^{2-} sites, the low temperature α -Zn₄Sb₃ phase may still be formulated⁴ as $(\text{Zn}^{2+})_{13}(\text{Sb}^{3-})_6(\text{Sb}_2^{4-})_2$, and the ratio of the Sb^{3-} to Sb^{2-} sites remains 3:2 in both phases.

The exceptionally low thermal conductivity of β -Zn₄Sb₃ has been ascribed¹ to the high degree of intricate disorder in the zinc portion of this compound. In contrast, the α -Zn₄Sb₃ phase⁴ is a completely ordered phase. The complete understanding and the improvement of the thermoelectric properties resulting from the complex disorder found in β -Zn₄Sb₃ 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 α - Zn_4Sb_3 and the β - Zn_4Sb_3 phases.

Antimony-121 Mössbauer spectroscopy is an ideal technique^{5–7} 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 α - Zn_4Sb_3 phase, a phase that must be characterized with as much accuracy as possible before the highly disordered β - Zn_4Sb_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.⁸ The $\text{Zn}_{3.97}\text{Sb}_3$ stoichiometry is in the middle of the experimental stability range for Zn_4Sb_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 CaSnO_3 and was calibrated at room temperature with α -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 α - Zn_4Sb_3 Mössbauer spectral absorber thickness, which is 32 mg/cm² of sample, 18.7 mg/cm² of natural abundance antimony, or 10.7 mg/cm² 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.⁹ 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 CaSnO_3 source, values which are identical to those given relative to BaSnO_3 .

Results and Discussion

The antimony-121 Mössbauer spectra of α - Zn_4Sb_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

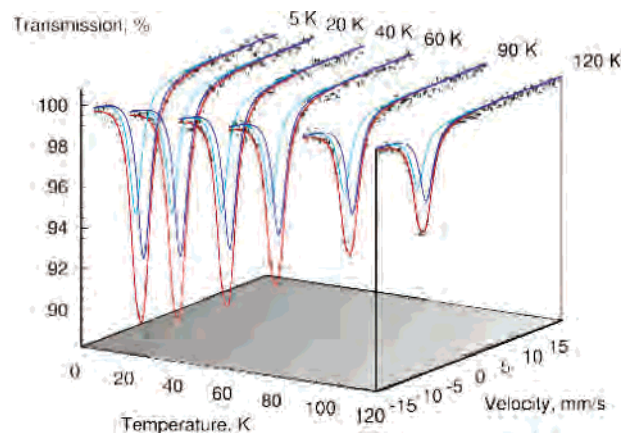


Figure 1. Mössbauer spectra of α - Zn_4Sb_3 obtained between 5 and 120 K. Sb^{3-} and Sb^{2-} spectral components are represented by the dark blue and cyan lines, respectively.

Mössbauer temperature of 197 K. Because, in this valence semiconductor, antimony is expected^{1–4} to be present as Sb^{3-} and 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 sites³ occupied by Sb^{3-} and 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 Sb^{3-} and 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,^{3,4} α - Zn_4Sb_3 has antimony in two different formal oxidation states, namely, Sb^{3-} and Sb^{2-} , states whose occupancies are in a 3:2 ratio. Second, the 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 Sb^{3-} and 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 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 Sb^{3-} and Sb^{2-} sites, the quadrupole interaction for the 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 χ^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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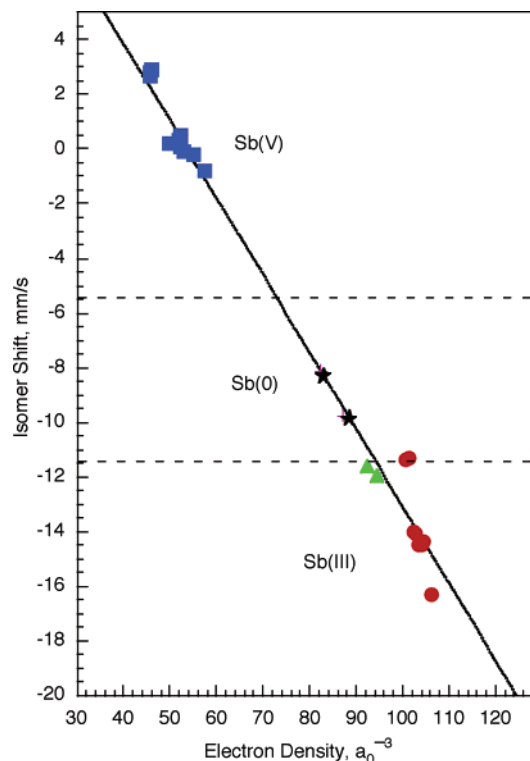


Figure 2. Correlation between the experimental values of the antimony-121 Mössbauer effect isomer shift, relative to CaSnO₃, and the calculated values of the electron density at the nucleus for the Sb(V), squares, Sb(0), triangles and pluses, and Sb(III), circles, compounds. The data is taken from refs 11 and 12. The stars correspond to α -Zn₄Sb₃.

the isomer shift is permitted to vary within the second-order Doppler shift model¹⁰ 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 α -Zn₄Sb₃ 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 observed⁷ 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

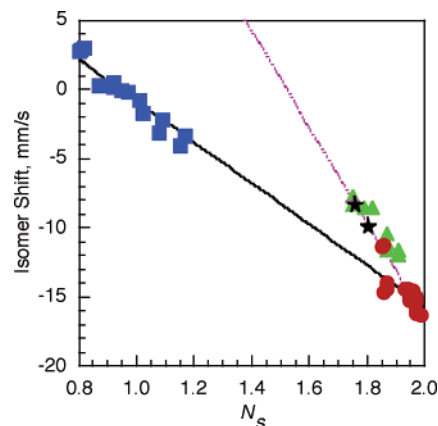


Figure 3. Correlation between the experimental values of the antimony-121 Mössbauer effect isomer shift, relative to CaSnO₃, and the calculated number of antimony 5s electrons, N_s , for the Sb(V), squares, Sb(0), triangles, and Sb(III), circles, compounds. The solid line represents a fit to the Sb(V) 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 α -Zn₄Sb₃.

CaSnO₃ were obtained for the Sb³⁻ and Sb²⁻ sites, respectively. A quadrupole interaction of -4.9(2) mm/s was obtained for the Sb³⁻ sites. A release of the constrained zero quadrupole interaction for the Sb²⁻ 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 observed⁷ in InSb at 90 K and, no doubt, reflects the existence of several crystallographic sites for both the Sb³⁻ and the Sb²⁻ contributions.

The isomer shifts observed for the two components occur in the range of the isomer shifts observed^{11,12} 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 Sb³⁻ and Sb²⁻ ions, respectively. The formal electronic configurations of the Sb³⁻ and Sb²⁻ ions are 5s²5p⁶ and 5s²5p⁵ 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^{7,11} of Sb(V) and Sb(III) compounds and, as a dotted line, the secondary screening effect of the 5p electrons in a series^{7,11,12} 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 formulated⁴ 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 Sb^{3-} and 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 Sb^{3-} and 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 expected⁴ 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 Sb^{3-} and 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 Sb^{3-} and 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 Sb^{3-} and Sb^{2-} ions, respectively. These two sets of electronic configurations constitute limiting values for the Sb^{3-} and Sb^{2-} ions and can be compared with the results³ of electronic structure calculations in $\beta\text{-Zn}_{13}\text{Sb}_{10}$. These calculations indicate that the 5s states of both the Sb^{3-} and the Sb^{2-} ions are fully occupied at approximately -11 eV below the Fermi level and that the 5p states of both the Sb^{3-} and the 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, $(\text{Zn}^{2+})_{13}(\text{Sb}^{3-})_6(\text{Sb}^{2-})_2$, as predicted¹³ by the Zintl formalism.

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

Debye model for the recoil-free fraction.¹⁴ Two Mössbauer temperatures, Θ_M , of 197(5) and 207(5) K have been obtained for the Sb^{3-} and 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 obtained¹⁷ 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 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 found⁶ in $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$, and values^{7,18} of 175(4) and 160(5) K were found for InSb . In contrast, the Mössbauer temperatures obtained herein are somewhat larger than the values of 165 to 180 K obtained¹⁷ for antimony metal but are similar to the Debye temperatures of 204 to 211 K determined¹⁹ 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 Sb^{3-} and 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 Sb^{3-} and Sb^{2-} ions, respectively, are in excellent agreement with band structure calculations³ and the Zintl formalism¹³ applied to this valence semiconductor. Furthermore, this simultaneous fit provides the Mössbauer lattice temperatures of the Sb^{3-} and 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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