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## Article

# Antimony-121 Mössbauer Spectral Study of the $Eu_{14}MnSb_{11}$ and $Yb_{14}MnSb_{11}$ Zintl Compounds

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The antimony-121 Mössbauer spectra of the $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$ Zintl compounds have been measured between 2 or 5 and 300 K. The resulting three-dimensional arrays of the spectral counts, velocity, and temperature have been simultaneously fit with a minimum number of free parameters. These fits yield a 0 Kelvin transferred hyperfine field of 2.9(2) T, a Curie temperature of 57(3) K, and a Mössbauer temperature of 182(2) K for $Yb_{14}$-$MnSb_{11}$; in this case the transferred field arises solely from the ordering of $Mn^{2+}$. Because $Eu_{14}MnSb_{11}$ has both $Eu^{2+}$ and $Mn^{2+}$ ions that are magnetically ordered, its antimony-121 Mössbauer spectra are more complex and reveal two magnetic transitions, the first at 92(1) K resulting from the ordering of the $Mn^{2+}$ ions and the second at 9.5(1.0) K resulting from the ordering of the $Eu^{2+}$ ions; the corresponding 0 Kelvin transferred hyperfine fields are 1.3(1) and 3.7(1) T. The antimony-121 isomer shifts yield electronic configurations of $5s^{1.74}5p^{4.28}$ and $5s^{1.74}5p^{4.19}$ for the average antimony anion in $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$, respectively.

## Introduction

The magnetic and transport properties of $Yb_{14}MnSb_{11}$ are of particular interest both because it has electronic properties similar to the InSb semiconductor and because it contains $Mn^{2+}$ ions that are magnetically ordered below 60 K. Because the $Mn^{2+}$ ions comprise only 4% of the ions present, $Yb_{14}$-$MnSb_{11}$ is promising as a potential dilute magnetic semiconductor and has been shown[1] to display Kondo effects and exhibit useful magnetoresistive and high-temperature thermoelectric properties.[2,3] Thus, $Yb_{14}MnSb_{11}$ may have uses

that vary from spintronic to thermopower devices. In addition, $Yb_{14}MnSb_{11}$ shows unusually complex behavior for such a simple magnetic compound.[4,5] In contrast, in $Eu_{14}$-$MnSb_{11}$ both $Eu^{2+}$ and $Mn^{2+}$ ions carry magnetic moments and $Eu_{14}MnSb_{11}$ orders[6] ferromagnetically below 92 K and exhibits a second magnetic transition at ca. 15 K. Europium-151 Mössbauer spectra have shown[7] that this second transition is related to the magnetic ordering of the $Eu^{2+}$ ions.

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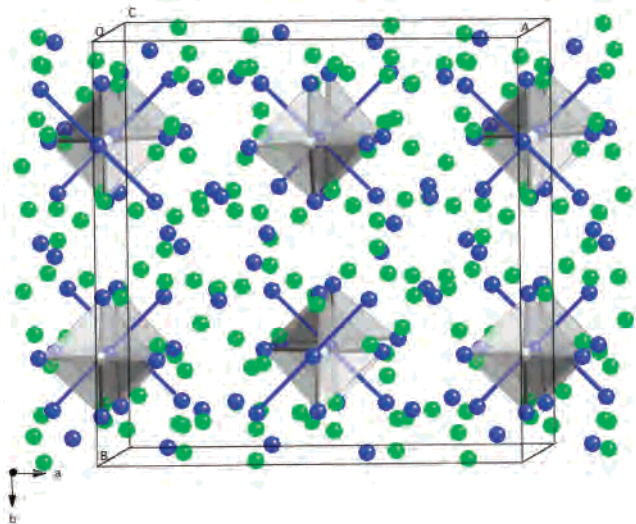(6) Chan, J. Y.; Wang, M. E.; Rehr, A.; Kauzlarich, S. M. *Chem. Mater.* **1997**, *9*, 2131−2138.

**Figure 1.** View of the crystal structure[6] of Yb$_{14}$MnSb$_{11}$. The Eu$^{2+}$ or Yb$^{2+}$ ions are shown in green, the Mn$^{2+}$ ions in light gray at the center of their antimony tetrahedra shown in gray, and the antimony ions in blue where the blue lines show the linear Sb$_3^{7-}$ chains.

Indirect probes of the magnetic system, such as replacing some Eu$^{2+}$ with a nonmagnetic alkaline-earth ion, have revealed[8,9] preferential site substitution and changes in the magnetic spin arrangement, the Curie temperature, the magnetic easy axis, and the electric properties with increasing alkaline-earth content.

Both Yb$_{14}$MnSb$_{11}$ and Eu$_{14}$MnSb$_{11}$ crystallize with the tetragonal $I4_1/acd$ crystal structure,[3,6] see Figure 1, and contain 208 ions per unit cell, including 88 antimony ions. Each formula unit contains 14 Yb$^{2+}$ or Eu$^{2+}$ ions, four-isolated Sb$^{3-}$ ions, one Sb$_3^{7-}$ linear chain, and one distorted MnSb$_4^{9-}$ tetrahedron, where the valence assignments are based on the Zintl–Klemm formalism.[3,10]

Local spin density calculations on $A_{14}$MnBi$_{11}$, where $A$ is Ca or Ba, predict the presence of a magnetically polarized hole localized on the MnBi$_4$ tetrahedron, a hole which is magnetically coupled parallel with the Mn$^{2+}$ local moment.[11] This is consistent with X-ray magnetic circular dichroism measurements on Yb$_{14}$MnSb$_{11}$, which show that Yb$^{2+}$ carries no moment, Mn$^{2+}$ has a 3d$^5$ electronic configuration, and that there exists a small moment on the antimony[3] Sb2 found in the MnSb$_4^{9-}$ tetrahedron, a moment which is antiparallel with the moment on the Mn$^{2+}$. Hence, the "magnetic unit" in the $A_{14}$MnSb$_{11}$ compounds is the MnSb$_4$ tetrahedra, with a magnetic moment of 4 $\mu_B$ composed of two contributions, a 5 $\mu_B$ moment arising from the fully occupied majority spin 3d valence electrons of manganese, and a $-1$ $\mu_B$, a moment of reversed polarization, arising from the 5p states of the four antimony in the MnSb$_4$ tetrahedron. These tetrahedra form two different, interpenetrating, three-dimensional sublattices with ferromagnetic coupling within each sublattice and possible antiferromagnetic coupling between tetrahedra from different sublattices. This model is also consistent with the observation[4] of a new magnetic anomaly in Yb$_{14}$MnSb$_{11}$, an anomaly that most likely results from a disruption of the ferromagnetic coupling between the sublattices by a small ac magnetic field.

Because the "magnetic unit" in the $A_{14}$MnSb$_{11}$ compounds involves the antimony in the MnSb$_4$ tetrahedra, an antimony-specific study of the magnetic properties of these compounds is compelling. Antimony-121 Mössbauer spectroscopy[12,13] provides this selectivity by probing both the electronic configurations of antimony ions and the transferred hyperfine fields they experience as a result of the surrounding magnetic ordering. In both Yb$_{14}$MnSb$_{11}$ and Eu$_{14}$MnSb$_{11}$ the antimony ions experience the magnetic ordering of the MnSb$_4$ tetrahedra, whereas in Eu$_{14}$MnSb$_{11}$ they also experience the additional magnetic ordering of the Eu$^{2+}$ ions.

Herein we report the electronic and magnetic properties of both Eu$_{14}$MnSb$_{11}$ and Yb$_{14}$MnSb$_{11}$ as determined from the temperature dependence of their antimony-121 Mössbauer spectra.

## Experimental Section

Yb$_{14}$MnSb$_{11}$ was prepared in a tin flux reaction as described earlier,[3] and Eu$_{14}$MnSb$_{11}$ was prepared with a stoichiometric mixture of the elements sealed in a quartz jacketed tantalum tube;[6] both compounds are the same samples as those used in earlier work.[3,7]

The Mössbauer spectra of Eu$_{14}$MnSb$_{11}$ and Yb$_{14}$MnSb$_{11}$ have been obtained in transmission geometry with a constant acceleration spectrometer. The Ca$^{121}$SnO$_3$ source was maintained at room temperature, and the isomer shifts are reported relative to CaSnO$_3$. CaSnO$_3$ has an isomer shift of +8.55(3) mm/s relative to InSb, the standard reference material for antimony-121 Mössbauer spectroscopy. The velocity scale was calibrated using $\alpha$-iron foil and a room-temperature cobalt-57 in Rh source.

The antimony-121 Mössbauer spectra have been simultaneously fit as a three-dimensional array of spectral counts, velocity, and temperature with a locally developed program that utilized the standard Levenberg–Marquardt minimization routine and was implemented in the gnufit package of programs. These fits used a Lorentzian line shape, and the temperature dependence of the thickness broadening was accounted for through a linear expansion of the line width, $\Gamma(T) = \Gamma_0 + c \log[A(T)]$, where $c$ is a weighting coefficient, $A$ is the spectral absorption area, and $\Gamma_0$, the limiting, experimentally observed, thin absorber line width, has been fixed herein at 2.7 mm/s. The fit is accomplished by defining the proper function, $f(x,y)$, for the two variables, velocity, $x$, and the temperature $T$, such that $f(x,T)$ is the Mössbauer spectrum obtained at a given temperature. The fit parameters that are used in a conventional Mössbauer spectral fit are replaced by their parametrized temperature dependence, the parameters of which are fitted to obtain the best simultaneous fit of all the spectra.[14]

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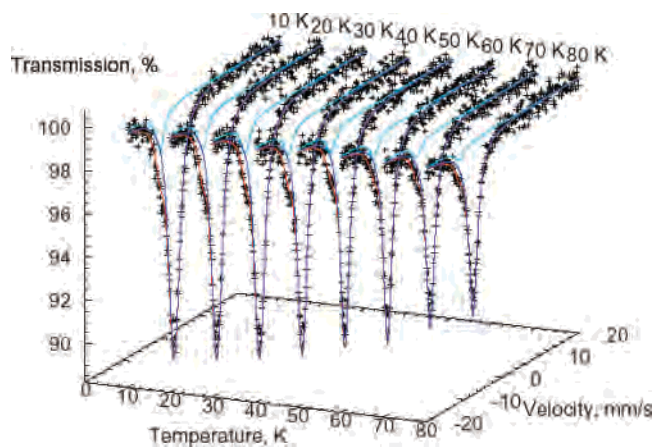(14) Details of this fitting routine may be obtained from r.hermann@fz.juelich.de.

**Figure 2.** Three-dimensional array of the simultaneously fit Sb-121 Mössbauer spectra of $Yb_{14}MnSb_{11}$. The red, cyan, and blue lines correspond to the total fit, $Sb_2O_3$ component, and $Yb_{14}MnSb_{11}$ component, respectively.



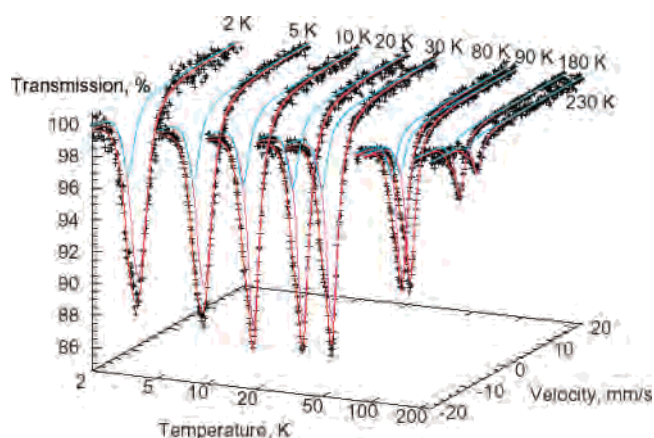**Figure 3.** Three-dimensional array of the simultaneously fit Sb-121 Mössbauer spectra of $Eu_{14}MnSb_{11}$. The red, cyan, and purple lines correspond to the total fit, $Sb_2O_3$ component, and $Eu_{14}MnSb_{11}$ component, respectively.

## Results and Discussion

The antimony-121 Mössbauer spectra of $Eu_{14}MnSb_{11}$ and $Yb_{14}MnSb_{11}$, obtained between 2 or 5 and 300 K have been simultaneously fit as a three-dimensional array of spectral counts, velocity, and temperature; the results obtained for $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$ are shown in Figures 2 and 3, respectively, and several individual spectral fits are also shown in Figure 4. Two spectral components have been used in these fits: a major component with a temperature-independent isomer shift of either $-7.68(1)$ or $-7.77(1)$ mm/s, assigned to $Yb_{14}MnSb_{11}$ or $Eu_{14}MnSb_{11}$, respectively, and a minor component with a temperature-independent isomer shift of $-11.4(1)$ or $-10.4(1)$ mm/s assigned[15] to an $Sb_2O_3$-like impurity; cubic $Sb_2O_3$ exhibits[16] an isomer shift of $-11.3(1)$ mm/s relative to $CaSnO_3$. Because both $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$ exhibit so many X-ray diffraction peaks, diffraction peaks resulting from small amounts of simple oxide impurities, such as $Sb_2O_3$, are probably indistinguishable from the compound and may well be present. It is also highly probable that any oxide may be
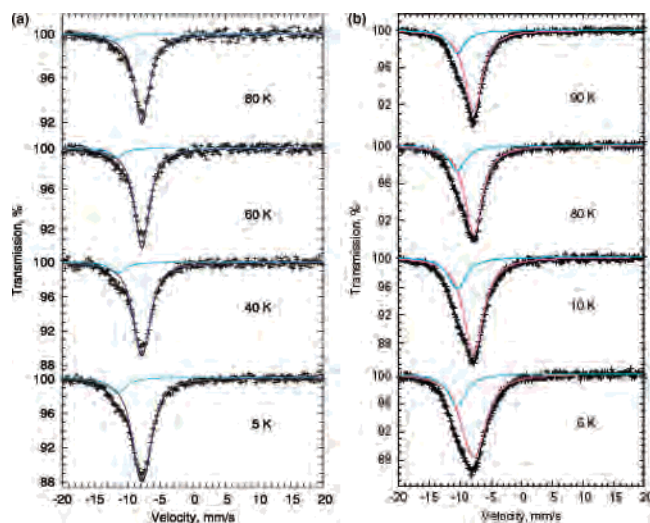
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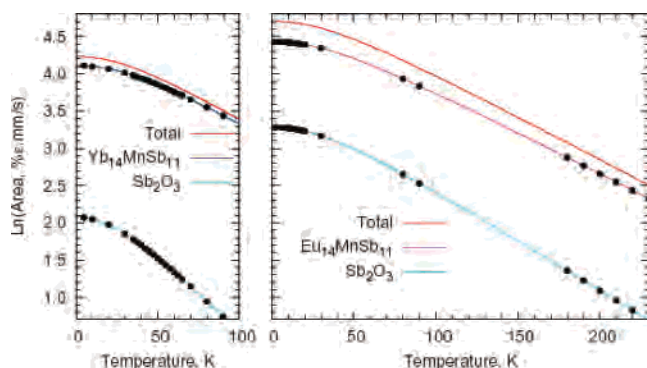
**Figure 4.** Several Sb-121 Mössbauer spectra of $Yb_{14}MnSb_{11}$ (a) and $Eu_{14}MnSb_{11}$ (b) obtained at the indicated temperatures. The cyan, blue, and purple lines correspond to $Sb_2O_3$, $Yb_{14}MnSb_{11}$, and $Eu_{14}MnSb_{11}$, respectively.

amorphous to X-rays and undetected. Further, previous experience[3,7,10,15] indicates that the surface of particles of similar Zintl-like compounds is very sensitive to oxidation with time. Apparently because of the delay between the preparation of $Yb_{14}MnSb_{11}$ or $Eu_{14}MnSb_{11}$ and their subsequent Sb-121 Mössbauer spectral study some of the surface of their particles has been oxidized. It is also possible that the oxide impurity has always been present in an amorphous form undetected by X-ray diffraction. From the isomer shifts it would appear that the impurity in $Yb_{14}MnSb_{11}$ is essentially $Sb_2O_3$ whereas in $Eu_{14}MnSb_{11}$ the impurity may contain at least some europium replacing the antimony in $Sb_2O_3$.

Unfortunately, because of the intrinsically broad line width of the Sb-121 Mössbauer-effect nuclear transition, it is impossible to resolve the spectral absorption lines associated with the four different antimony sites in $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$, each of which may have slightly different isomer shifts, quadrupole interactions, and hyperfine fields. The presence of the $Sb_2O_3$ impurity adds further problems, and thus, the spectral fits have been limited to determining the average isomer shift and average hyperfine field of the four crystallographically different antimony sites found in $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$. In the simultaneous fits the temperature dependence of the absorption area of each spectral component has been constrained to be consistent with the Debye model for which two parameters are fit, the asymptotic zero temperature spectral absorption area and the Mössbauer temperature. Further, the temperature dependence of the line width of the two components has been constrained to take into account any thickness broadening at low temperature. The thin absorber line width has been fixed at 2.7 mm/s, a value which is typical for the absorber thickness and the spectrometer used herein.

Below 55 K the major component in the spectra of $Yb_{14}MnSb_{11}$ has been fit with a hyperfine field and a zero quadrupole interaction. The hyperfine field has been constrained to have a Brillouin dependence with $S = 5/2$, a dependence that involves two fitting parameters, the zero

**Figure 5.** Temperature dependence of the absorption area of the Sb-121 Mössbauer spectra of Yb₁₄MnSb₁₁ (a) and Eu₁₄MnSb₁₁ (b).

temperature hyperfine field and the Curie temperature. This hyperfine field results from the magnetic moment present on the MnSb₄ tetrahedral magnetic unit in which the $Mn^{2+}$ cations carry a magnetic moment of 5 $\mu_B$ and is expected to follow an $S = 5/2$ Brillouin temperature dependence. The influence of the small magnetic moment shared by the four antimony anions around the manganese cation has been neglected in the present fitting model, but we note that fits constrained to follow an $S = 2$ Brillouin temperature dependence would be essentially the same.

Close examination of the spectra of Eu₁₄MnSb₁₁ indicates a broadening of the spectrum at and below 90 K, a broadening that is no doubt related to the magnetic ordering of the compound or at least of the MnSb₄ tetrahedra. An additional broadening of the spectra occurs below 15 K, a broadening that is no doubt related to the ordering of the $Eu^{2+}$ ions. These broadened spectra have been fit with an additional hyperfine field and a zero quadrupole interaction. The hyperfine field transferred from the magnetic $Eu^{2+}$ ions has been constrained to follow a Brillouin dependence with $S = 7/2$ as would be expected for $Eu^{2+}$.

In summary, the 19 spectra of Yb₁₄MnSb₁₁ and 24 spectra of Eu₁₄MnSb₁₁ have been fit simultaneously with a minimum number of free parameters, each of which has a physical meaning. These parameters are one thickness broadening line width parameter, two Mössbauer temperatures, two isomer shifts, one or two hyperfine fields, one or two ordering temperatures, the total spectral absorption area at zero temperature, and the fractional area of the minority component. Yb₁₄MnSb₁₁ and Eu₁₄MnSb₁₁ have been found to contain ca. 11% and 25% of an Sb₂O₃ impurity, the weak component shown in the spectral fits. As shown in Figures 2−4, all spectral fits are very good to excellent.

The temperature dependence of the logarithm of the absorption area for Yb₁₄MnSb₁₁ or Eu₁₄MnSb₁₁ and for the Sb₂O₃ impurity is shown in Figure 5. The Mössbauer temperatures obtained for Yb₁₄MnSb₁₁ and Eu₁₄MnSb₁₁ are 182(2) and 194(2) K, and the Mössbauer temperature for the impurity is 148(4) and 176(2) K. The former temperatures are similar to the observed values of 160(5) K in InSb, 201-(1) K in Eu₁₀Mn₆Sb₁₃, and 200(5) K in Zn₄Sb₃ and typical of the lattice rigidity found in antimony-containing intermetallic compounds. The Mössbauer temperature of 182(2) K obtained for Yb₁₄MnSb₁₁ is also in rather good agreement
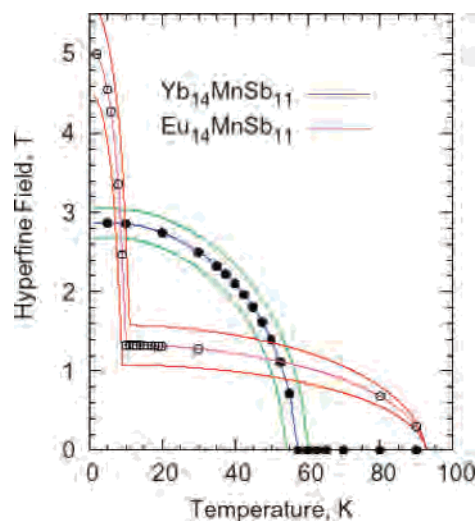


**Figure 6.** Temperature dependence of the hyperfine field observed in Yb₁₄-MnSb₁₁ and Eu₁₄MnSb₁₁. The blue line corresponds to a fit with a 0 Kelvin hyperfine field of 2.9(2) T and a Curie temperature of 57(3) K for Yb₁₄-MnSb₁₁. The purple line corresponds to a fit with a 0 Kelvin hyperfine field of 1.3(2) T and a Curie temperature of 92 K between 10 and 90 K and with a 0 Kelvin hyperfine field of 3.7(1) T and a transition temperature of 9.5(1.0) K below 10 K for Eu₁₄MnSb₁₁. The green and red lines correspond to a 2σ error in the hyperfine fields and transition temperatures.

with its Debye temperature, which has been estimated[17] to be 160(10) K.

The temperature dependence of the hyperfine field in Yb₁₄-MnSb₁₁ and Eu₁₄MnSb₁₁ is shown in Figure 6. The fitted Curie temperature is 57(3) and 92(1) K for Yb₁₄MnSb₁₁ and Eu₁₄MnSb₁₁, respectively. These values agree well with the Curie temperatures of 53 or 52(1) and 92 K obtained from magnetic measurements.[4,7,10] The temperature of the onset of the second magnetic transition in Eu₁₄MnSb₁₁ is 9.5(1.0) K and somewhat smaller than the reported[6] value of 15 K. The 0 Kelvin transferred hyperfine field from the $Mn^{2+}$ ions or the MnSb₄ tetrahedral magnetic moiety in Eu₁₄MnSb₁₁ and Yb₁₄MnSb₁₁ is 1.3(2) and 2.9(2) T, respectively. The additional 0 Kelvin transferred hyperfine field from the $Eu^{2+}$ ions in Eu₁₄MnSb₁₁ is 3.7(1) T and results in a total 0 Kelvin transferred field of 5.0(2) T.

In fitting the Mössbauer spectra of Eu₁₄MnSb₁₁, the two transferred fields have been assumed to have the same sign. The alternative approach, in which the two transferred fields were assumed to be opposite in sign, was tried and led to equally good fits, with 0 Kelvin fields of 1.0(1) and 6.1(1) T and transition temperatures of 92(1) and 11(1) K. All other fitted parameters are not significantly different from those reported above. Hence, the antimony-121 Mössbauer spectra cannot distinguish between these two possibilities for the sign of the transferred field unless spectra had been collected at many temperatures in the region of the possible compensation of the two transferred fields.

In both Yb₁₄MnSb₁₁ and Eu₁₄MnSb₁₁ the transferred hyperfine fields are very small and smaller than the transferred fields measured in several intermetallic compounds. For instance, a transferred field of 8.3(1) T was

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observed[12] in $Eu_{10}Mn_6Sb_{13}$, fields of ca. 30 T were observed[18] in both PdMnSb and NiMnSb, and a field of $\sim$36 T was observed in MnSb.[19] The comparison between $Yb_{14}MnSb_{11}$ and NiMnSb is particularly interesting in view of the magnetic circular dichroism results obtained on these compounds. Both compounds show dichroic signals on both manganese and antimony. However, the dichroic signals on manganese and antimony are of opposite sign[3] in $Yb_{14}$-$MnSb_{11}$ and the same sign[20] in NiMnSb. This difference occurs because the manganese cations are in an octahedral crystal field in NiMnSb and a tetrahedral crystal field in $Yb_{14}$-$MnSb_{11}$. Hence, the manganese and antimony spins are parallel in NiMnSb, whereas they are antiparallel in $Yb_{14}$-$MnSb_{11}$. The large difference in transferred field on the antimony in $Yb_{14}MnSb_{11}$ and NiMnSb is most certainly related to the tetrahedral geometry around the manganese cation, a geometry that is less favorable than the octahedral geometry for the spin-polarization transfer from the manganese to the antimony and leads to the antiparallel alignment[5,11] of the manganese and antimony spins.

As indicated above, because of the intrinsic broad line width of the antimony-121 Mössbauer-effect transition, all four crystallographically different antimony sites in $Yb_{14}$-$MnSb_{11}$ and $Eu_{14}MnSb_{11}$ have been fit with one component in the spectral analysis. In both compounds only one of the four crystallographic antimony sites, the Sb2 site, participates in the $MnSb_4$ magnetic unit, a unit that forms two ferromagnetic sublattice networks that are probably weakly magnetically coupled to each other.[11] The assumption that all antimony anions experience the same transferred field from the $MnSb_4$ magnetic unit may also contribute a small underestimation of the transferred field. Further, the ferromagnetic coupling within the sublattices, when combined with more efficient transfer due to the lanthanide contraction, may account for the larger transferred field of 2.9(2) T observed in the "smaller" $Yb_{14}MnSb_{11}$ as compared to the field of 1.3(1) T observed in the "larger" $Eu_{14}MnSb_{11}$. In contrast, all the antimony sites in $Eu_{14}MnSb_{11}$ have eight $Eu^{2+}$ near neighbors and thus directly experience a total transferred field of 5.0(2) T. Finally, as expected, the antimony-121 Mössbauer spectra do not reveal any evidence for the two magnetic sublattices[1] reported in $Yb_{14}MnSb_{11}$ nor for their antiferromagnetic or ferromagnetic coupling.

The Zintl formalism indicates that the average antimony ion in $Yb_{14}MnSb_{11}$ or $Eu_{14}MnSb_{11}$ has a charge of $-2.73$. The average antimony-121 isomer shifts observed for $Yb_{14}$-$MnSb_{11}$ and $Eu_{14}MnSb_{11}$ are the most positive isomer shifts reported for zero valence antimony in a semiconducting compound. AlSb has an isomer shift of $-7.8$ mm/s, an isomer shift that corresponds to an electronic configuration $5s^{1.75}5p^{3.44}$ for antimony and a valence electron density at

the nucleus of 85.6 $a_0^{-3}$. For comparison, antimony metal, which has been reported[21−23] to exhibit an isomer shift between $-11.3$ and $-11.95$ mm/s, has a far more negative isomer shift than $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$.

From the known[15] linear correlation of the isomer shift and the electron densities at the antimony-121 nucleus a value of 80.8 and 81.2 $a_o^{-3}$, where $a_o$ is the Bohr radius, is obtained for $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$, respectively. The combined influence of $N_s$ and $N_p$, the number of 5s and 5p electrons on the electron density at the antimony nucleus, $\rho(0)$, has been formulated[24] as

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

Using the above determined electron density at the antimony-121 nucleus and the assumption that the average antimony anion in $Yb_{14}MnSb_{11}$ has two 5s electrons, eq 1 yields an $N_p$ value larger than six, a value that is, of course, unacceptable. This indicates that the average antimony electronic configuration is close to $5s^25p^6$ and that the average antimony anion is close to $Sb^{3-}$. If the screening of the 5p electrons is taken into account, then a limiting electron configuration of $5s^{1.74}5p^{4.28}$ and $5s^{1.74}5p^{4.19}$ is obtained for the average antimony anion in $Yb_{14}MnSb_{11}$ and $Eu_{14}MnSb_{11}$, respectively. The two limiting electron configurations indicate that the antimony valence is between $-1$ and $-3$, in reasonable agreement with the average charge given by the Zintl formalism. The electronic configuration of $5s^{1.74}5p^{4.28}$ is certainly consistent with the observation[3] of a 3d to 5p transition in the antimony $M_{45}$ X-ray absorption spectrum of $Yb_{14}MnSb_{11}$, whereas the $5s^25p^6$ electronic configuration would be inconsistent.

**Note Added after ASAP Publication.** This paper was released ASAP on November 7, 2007, without a current address for one of the authors. The corrected version was posted on November 13, 2007.

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