Magnetic Investigations and ^{151}Eu Mössbauer Spectroscopy of MYbSi$_4$N$_7$ with M = Sr, Ba, Eu

Henning A. Höppe[a,b], Henning Trill[c], Gunter Kotzyba[a], Bernd D. Mosel[c], Rainer Pöttgen[d], and Wolfgang Schnick[a,*]

[a] München, Department Chemie der Ludwig-Maximilians-Universität
[b] Oxford / United Kingdom, Inorganic Chemistry Laboratory, University of Oxford
Münster, [c] Institut für Physikalische Chemie and [d] Institut für Anorganische und Analytische Chemie der Universität Münster

Abstract. The isotypic nitridosilicates MYb[Si$_4$N$_7$] (M = Sr, Ba, Eu) were obtained by the reaction of the respective metals with Si(NH)$_2$ in a radiofrequency furnace below 1600 °C. On the basis of powder diffraction data of MYb[Si$_4$N$_7$] Rietveld refinements of the lattice constants were performed; these confirmed the previously published single-crystal data. The compounds contain a condensed network of corner-sharing [N(SiN$_3$)$_4$] units. The central nitrogen thus exhibits ammonium character. Magnetic susceptibility measurements of MYb[Si$_4$N$_7$] (M = Sr, Ba, Eu) show paramagnetic behavior with experimental magnetic moments of 3.03(2), (Sr), 2.73(2) (Ba), and 9.17(2) (Eu) μ_B per formula unit. In EuYbSi$_4$N$_7$ the europium and ytterbium atoms are in stable divalent and trivalent states, respectively. According to the non-magnetic character of the alkaline earth cations, ytterbium has to be in an intermediate valence state Yb$^{III\text{-}x}$ in the strontium and barium compound. Consequently, either a partial exchange N^{3-}/O^{2-} resulting in compositions MYb$^{III\text{-}x}$[Si$_4$N$_{7-x}$O$_x$] or an introduction of anion defects according to MYb$^{III\text{-}x}$[Si$_4$N$_{7-x/3}\square_{x/3}$] has to be assumed. The phase width $0 \leq x \leq 0.4$ was estimated according to the magnetic measurements. ^{151}Eu Mössbauer spectra of EuYb[Si$_4$N$_7$] at 78 K show a single signal at an isomer shift of $\delta = -12.83(3)$ mm s^{-1} subject to quadrupole splitting of $\Delta E_Q = 5.7(8)$ mm s^{-1}, compatible with purely divalent europium.

Keywords: Mössbauer spectroscopy; Magnetic properties, Intermediate valency

Magnetische Untersuchungen und ^{151}Eu-Mössbauer-Spektroskopie an MYbSi$_4$N$_7$, M = Sr, Ba, Eu

Inhaltsübersicht. Die isotypen Nitridosilicate MYb[Si$_4$N$_7$] (M = Sr, Ba, Eu) wurden durch Reaktion der entsprechenden Metalle mit Si(NH)$_2$ in einem Hochfrequenzofen unterhalb von 1600 °C erhalten. Mit dem Rietveld-Verfahren wurden die Gitterkonstanten der Verbindungen MYb[Si$_4$N$_7$] verfeinert, welche die zuvor publizierten Einkristalldaten bestätigen. Die Verbindungen enthalten ein kondensiertes Netzwerk eckenverknüpfter [N(SiN$_3$)$_4$]-Einheiten, wobei dem zentralen N-Atom Ammoniumcharakter zukommt. Magnetische Suszeptibilitätsmessungen an MYb[Si$_4$N$_7$] (M = Sr, Ba, Eu) zeigen paramagnetisches Verhalten mit experimentellen magnetischen Momenten von 3,03(2) (Sr), 2,73(2) (Ba) und 9,17(2) (Eu) μ_B pro Formeleinheit. In EuYbSi$_4$N$_7$ liegen die Eu- bzw. Yb-Atome zwei- bzw. dreiwertig vor. Entsprechend dem nicht-magnetischen Charakter der Erdalkali-Ionen muss Ytterbium zwischenvalent als Yb$^{III\text{-}x}$ in der Strontium- und Bariumverbindung vorliegen. Folglich ergibt sich entweder ein partieller Austausch N^{3-}/O^{2-} gemäß MYb$^{III\text{-}x}$[Si$_4$N$_{7-x}$O$_x$] oder das Auftreten von Anionendefekten gemäß MYb$^{III\text{-}x}$[Si$_4$N$_{7-x/3}\square_{x/3}$]. Die Phasenbreite wurde aufgrund der magnetischen Messungen zu $0 \leq x \leq 0{,}4$ abgeschätzt. Die an EuYb[Si$_4$N$_7$] aufgenommenen ^{151}Eu-Mössbauer-Spektren zeigen bei 78 K ein einzelnes Signal bei der Isomerieverschiebung $\delta = -12{,}83(3)$ mm s^{-1} mit einer Quadrupolaufspaltung $\Delta E_Q = 5{,}7(8)$ mm s^{-1}. Es liegt somit ausschließlich Eu^{2+} vor.

1 Introduction

Nitridosilicates derive from the classical oxosilicates (which are made up of SiO$_4$ tetrahedra) by a formal exchange of oxygen by nitrogen. Thus they contain SiN$_4$ tetrahedra. This substitution results in a significant extension of the structural possibilities [1, 2]. For example, tertiary atoms N$^{[3]}$ have been identified in the series Ln_3[Si$_6$N$_{11}$] (Ln = La, Ce, Pr, Nd, Sm) [3−5] and quaternary atoms N$^{[4]}$ have been identified in the herein described nitridosilicates MYb[Si$_4$N$_7$] (M = Sr, Ba, Eu) and in oxonitridosilicates deriving from Er$_6$[Si$_{11}$N$_{20}$]O [6, 7]. Analogous structural connectivities of oxygen are unknown in oxosilicate chemistry. Nitridosilicates exhibit a high chemical and thermal stability and they are promising candidates for high performance applications. Our initial studies of the optical properties of the europium doped phases Ba$_{2-x}$Eu$_x$[Si$_5$N$_8$] revealed strong fluorescence, long lasting luminescence, thermoluminescence, and two-photon-excitation [8].

Recently, we have started a more systematic study of the magnetic behavior of rare earth metal based nitridosilicates. In Ba$_4$Pr$_7$[Si$_{12}$N$_{23}$O](BN$_3$) [9], Ho$_2$[Si$_4$N$_6$C] and Tb$_2$[Si$_4$N$_6$C] [10], the rare earth atoms are in a stable tri-

---

* Prof. Dr. W. Schnick
Department Chemie, Ludwig-Maximilians-Universität München
Butenandtstraße 5−13 (D)
D-81377 München, Germany
Fax: +49-(0)89-2180-77440
E-Mail: wolfgang.schnick@uni-muenchen.de

valent oxidation state. No magnetic ordering was observed down to 2 K. In $Ce_3[Si_6N_{11}]$ [11] the experimental magnetic moment of 2.10 μ_B is slightly reduced as compared with the free ion value of 2.54 μ_B for Ce^{3+}. Deviations from Curie-Weiss behavior below 100 K might be indicative for crystal field splitting of the $J = 5/2$ ground state of the Ce^{3+} ion. Paramagnetic behavior of the divalent europium ions was observed in $Eu_2Si_5N_8$ [12, 13]. Interestingly, this nitridosilicate shows ferromagnetic ordering at 13 K.

We have now focused on the magnetic properties of $EuYb[Si_4N_7]$ whose crystal structure has been elucidated recently [12]. The compound contains two different rare earth cations, which are potential candidates for mixed valency or valence changes, i. e. Eu^{II} [Xe]$4f^7$ vs. Eu^{III} [Xe]$4f^6$ and Yb^{II} [Xe]$4f^{14}$ vs. Yb^{III} [Xe]$4f^{13}$. According to the isotypic nitridosilicates $SrYb[Si_4N_7]$ and $BaYb[Si_4N_7]$ [14, 15] we expect divalent Eu and trivalent Yb. Up to now only divalent Eu has been found in nitridosilicates. We ascribe this to slightly reducing conditions during the synthesis when the pure metals react with the solid and polymeric "acid" silicon diimide $Si(NH)_2$ under evolution of hydrogen. Herein we report on magnetic susceptibility and ^{151}Eu Mössbauer spectroscopic measurements on MYb$[Si_4N_7]$ (M = Sr, Ba, Eu) to shed light on this issue.

2 Experimental Section

2.1 *Synthesis and X-ray powder data*

The syntheses of MYb$[Si_4N_7]$ (M = Sr, Ba, Eu) were performed in a radiofrequency furnace (type IG 10/200 Hy, frequency: 200 kHz, electrical output: 0-12 kW, Hüttinger, Freiburg) according to Eq. (1).

$$M + \mathrm{Yb} + 4\ \mathrm{Si(NH)_2} \rightarrow M\mathrm{Yb[Si_4N_7]} + 4\ \mathrm{H_2} + {}^1\!/_2\ \mathrm{N_2} \qquad (1)$$

Under argon a mixture of 30.4 mg (0.523 mmol) silicon diimide [16] and 17.4 mg (0.127 mmol) barium metal (ABCR, 99.9 %) and 23.0 mg (0.133 mmol) ytterbium metal (ABCR, 99.9 %) were transferred into a tungsten crucible. The latter was then heated under nitrogen to 1000 °C within 5 min in the water-cooled quartz-reactor of the radiofrequency furnace [17]. After 25 min the crucible was heated to 1600 °C within 12 h and held at this temperature for another 3 h. Then the mixture was cooled to 1000 °C within 3 h. Subsequent quenching to room temperature within 30 min yielded single phase $BaYb[Si_4N_7]$. Excess barium or ytterbium metal evaporated off the reaction mixture and condensed at the inner surface of the water-cooled quartz-reactor. $BaYb[Si_4N_7]$ was obtained as a coarsely crystalline, yellowish powder. More details about the experimental setup are given in references [17] and [18]. The syntheses of $SrYb[Si_4N_7]$ and $EuYb[Si_4N_7]$ were performed analogously using 11.1 mg (0.127 mmol) strontium metal (ABCR, 99.9 %), 20.9 mg (0.121 mmol) ytterbium metal and 130 mg (2.237 mmol) silicon diimide at a maximum temperature of 1600 °C and 86.5 mg (0.569 mmol) europium metal (ABCR, 99.9 %), 98.3 mg (0.568 mmol) ytterbium metal and 28.9 mg (0.498 mmol) silicon diimide at a maximum temperature of 1500 °C, respectively.

The purity of our samples was checked by X-ray powder diffraction (Stoe Stadi P) using Mo-Kα radiation. The Rietveld refinement of the lattice parameters (space group $P6_3mc$, no. 186) using the program GSAS [19] led to the values presented in Table 1. Excellent agreement with the previously published data [12, 14, 15] was found. The Rietveld fit of the X-Ray powder diffraction pattern of $BaYb[Si_4N_7]$ is shown in Fig. 1.

Table 1 Data of the Rietveld refinements of the lattice constants of the phases MYb$[Si_4N_7]$ (M = Sr, Ba, Eu); the refinements were performed using the program GSAS [19]

$EuYb[Si_4N_7]$	$SrYb[Si_4N_7]$	$BaYb[Si_4N_7]$
	$P6_3mc$ (no. 186)	
a = 599.408(6) pm	a = 599.73(2) pm	a = 603.119(8) pm
c = 977.18(2) pm	c = 978.14(3) pm	c = 983.70(2) pm
$V = 304.053(7) \cdot 10^6$ pm^3	$V = 304.68(2) \cdot 10^6$ pm^3	$V = 309.884(9) \cdot 10^6$ pm^3
$wR_P = 0.065$	$wR_P = 0.037$	$wR_P = 0.062$
$R_P = 0.053$	$R_P = 0.029$	$R_P = 0.049$
$R_{F^2 2} = 0.043$	$R_{F^2} = 0.091$	$R_{F^2} = 0.049$
$R_F = 0.032$	$R_F = 0.068$	$R_F = 0.031$
$\chi^2 = 0.60$	$\chi^2 = 2.42$	$\chi^2 = 0.78$
14 profile parameters	17 profile parameters	14 profile parameters
201 refl.	201 refl.	129 refl.
($2\theta_{max} = 60.0°$)	($2\theta_{max} = 60.0°$)	($2\theta_{max} = 50.0°$)

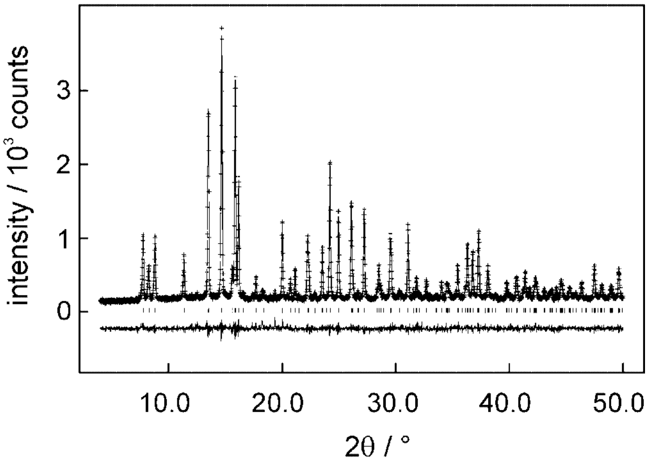

Fig. 1 Observed (crosses) and calculated (line) X-ray powder diffraction pattern (Mo-K$_\alpha$ radiation) as well as the difference profile of the Rietveld refinement of $BaYb[Si_4N_7]$. The row of vertical lines indicates possible peak positions of $BaYb[Si_4N_7]$.

2.2 *Physical property measurements*

The magnetic susceptibilities of polycrystalline, powdered samples of MYb$[Si_4N_7]$ (M = Sr, Ba, Eu) were measured with an MPMS *XL* SQUID magnetometer (Quantum Design) in the temperature range 4.2 to 300 K with magnetic flux densities up to 5 T. The quantities of the MYb$[Si_4N_7]$ (M = Sr, Ba, Eu) samples ranged between 2 and 25 mg. They were enclosed in small silica tubes and fixed at the sample holder rod. The sample was then cooled to 4.2 K in zero magnetic field and slowly heated to room temperature in an applied external field.

The 21.53 keV transition of ^{151}Eu with an activity of 130 MBq (2 % of the total activity of a $^{151}Sm{:}EuF_3$ source) was used for the Mössbauer spectroscopic experiment on $EuYb[Si_4N_7]$. The measurements were performed with a helium bath cryostat in the temperature range 4.2 to 300 K. The temperature of the absorber was varied while the source was kept at room temperature. The sample

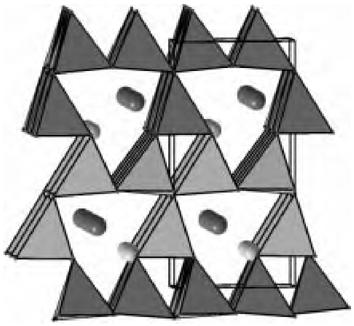

Fig. 2 Perspective view of the crystal structure of MYb[Si_4N_7] (M = Eu, Sr, Ba) along [100] (SiN_4 tetrahedra are shown as closed polyhedra, M: light gray, Yb: dark gray).

was diluted with sugar and placed within a thin-walled PVC container at a thickness corresponding to about 10 mg Eu cm^{-2}.

3 Results and Discussion

3.1 *Crystal chemistry*

The compounds MYb[Si_4N_7] (M = Sr, Ba, Eu) contain a condensed network of corner-sharing [$N(SiN_3)_4$] units. The central nitrogen represents the common vertex of four corner-sharing SiN_4 tetrahedra, and it thus exhibits ammonium character. The [Si_4N_7]$^{5-}$ network can be described as a defect stacking variant of wurtzite type AlN. Thus by systematic elimination of Si tetrahedral centers 6-ring channels along [100] are formed. The cations are situated in these channels (Fig. 2).

3.2 *Magnetic Properties and ^{151}Eu Mössbauer Spectroscopy*

The temperature dependence of the inverse magnetic susceptibilities of MYb[Si_4N_7] (M = Sr, Ba, Eu) is displayed in Fig. 3. The three compounds obey the Curie-Weiss law above 150 K, however, a slight convex curvature is observed, indicating temperature independent contributions. We have thus fitted the data of the whole temperature range with a modified Curie-Weiss expression $\chi = \chi_O + C/(T-\theta)$, accounting for the temperature independent contribution χ_O. The experimentally obtained magnetic data are summarized in Table 2.

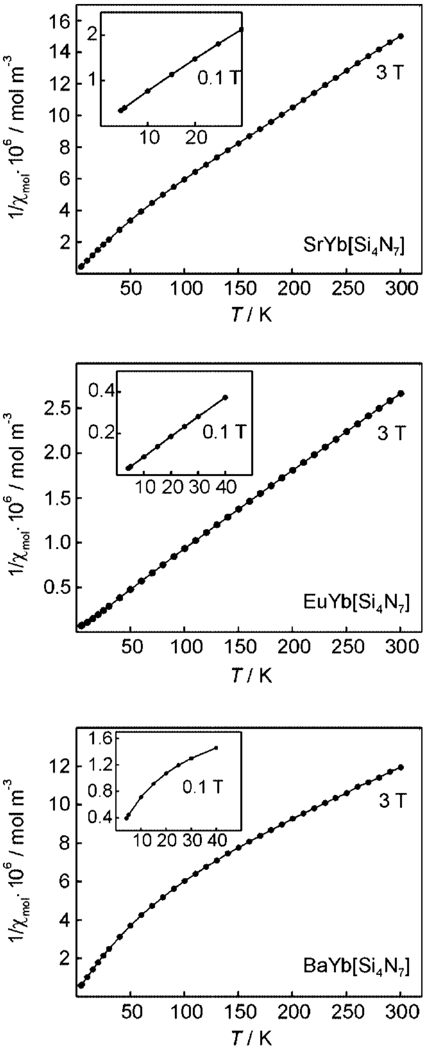

Fig. 3 Temperature dependence of the inverse magnetic susceptibilities of SrYb[Si_4N_7], EuYb[Si_4N_7] and BaYb[Si_4N_7] measured at a flux density of 3 T. The low-temperature behavior at 0.1 T is presented in the inserts.

Table 2 Magnetic data of MYb[Si_4N_7] (M = Sr, Ba, Eu): μ_{exp}: experimental magnetic moment per formula unit; χ_O: temperature independent part of the susceptibility; θ: paramagnetic Curie temperature (Weiss constant); $\mu_{sm(exp)}$: experimentally obtained saturation magnetization per formula unit

Compound	μ_{exp} / μ_B f.u.$^{-1}$	χ_O / m^3/mol	θ / K	$\mu_{sm(exp)}$ / μ_B f.u.$^{-1}$
SrYb[Si_4N_7]	3.03(2)	23(1) · 10^{-9}	−2.1(1)	1.53(2)
BaYb[Si_4N_7]	2.73(2)	50(1) · 10^{-9}	−2.7(1)	1.11(2)
EuYb[Si_4N_7]	9.17(2)	−132(1) · 10^{-9}	−4.9(2)	7.59(2)

First we will discuss the data of SrYb[Si_4N_7] and BaYb[Si_4N_7]. In a formal ionic description we can write $Sr^{2+}Yb^{3+}[Si_4N_7]^{5-}$. Consequently only the Yb^{3+} ions with the electronic configuration [Xe]$4f^{13}$ carry a paramagnetic moment. The free ion value of Yb^{3+} according to $\mu_{eff} = g[(J(J+1)]^{1/2}\ \mu_B$ is 4.54 μ_B [20]. The experimentally obtained magnetic moments per formula unit (f. u.) are significantly smaller than the free ion value, i. e. 3.03(2) μ_B for SrYb[Si_4N_7] and 2.73(2) μ_B for BaYb[Si_4N_7]. Thus, some of the ytterbium atoms are apparently divalent and diamagnetic, i. e. they have an electron configuration [Xe]$4f^{14}$. This however, may be achieved, if a small part of the nitride anions (N^{3-}) are replaced by oxide anions (O^{2-}) or anion defects in order to maintain charge balance. As a further possibility cation defects on the Yb position were taken in account though according to the Rietveld refinements this seems not to be very likely. Consequently, in the case of partial replacement of nitride anions by oxide anions a formula $SrYb^{III-x}[Si_4N_{7-x}O_x]$, and in the case of anion defects a formula $M$$Yb^{III-x}[Si_4N_{7-x/3}\square_{x/3}]$ with M = Sr, Ba has to be assumed. There are three crystallographically independent nitrogen atoms in the crystal structure of *M*Yb[Si_4N_7] [12, 14, 15]. One (N3) is the quaternary ammonium like position, the other two (N1 and N2) are connected to two silicon atoms each. Accordingly, the introduced oxygen atoms or anion defects are most likely positioned on the sites N1 and N2. This assignment was chosen because normally in oxonitridosilicates nitrogen, in comparison to oxygen, prefers the higher coordination number [18] towards silicon according to Pauling's rules [21].

Further possibilities to compensate the lack of positive charge are a partial introduction of defects on N positions or at those of Yb positions avoiding an intermediate valence state of Yb. The latter can be excluded by the Rietveld refinements, which was not indicative for a partial occupation of the cation positions. However Density Functional Theory (DFT) calculations confirm both intermediate valency of Yb and the partial substitution of N^{3-} by O^{2-} on sites N1 and N2 [22]. The phase width x was estimated by comparing the theoretically expected magnetic moments of the respective compounds with the experimental magnetic moments and hence amounts to x = 0.333(3) for $SrYb^{III\text{-}x}[Si_4N_{7-x}O_x]$/$SrYb^{III\text{-}x}[Si_4N_{7-x/3}\square_{x/3}]$ and to x = 0.399(3) for $BaYb^{III\text{-}x}[Si_4N_{7-x}O_x]$/$BaYb^{III\text{-}x}[Si_4N_{7-x/3}\square_{x/3}]$, respectively.

The magnetization behavior of SrYb[Si_4N_7] and BaYb[Si_4N_7] is shown in Fig. 4. At 50 K the magnetization isotherms are linear and the magnetizations at 5 T are around 0.2 μ_B per formula unit, as expected for a paramagnetic material. Although the susceptibility measurements gave no indication for magnetic ordering down to 2 K, we observe a stronger increase of the magnetization isotherms at 2 K. At 5 T the magnetizations are 1.53(2) μ_B / f. u. ($SrYbSi_4N_7$) and 1.11(2) μ_B / f. u. (BaYb[Si_4N_7]), significantly smaller than the theoretical saturation moment $\mu_{sm(calc)} = 4\ \mu_B$/Yb according to the relation $\mu_{sm(calc)} = g{\cdot}J\ \mu_B$ [20]. Thus, in the presence of an applied external magnetic field, some spins show a parallel alignment, resulting in the increased moment.

EuYb[Si_4N_7] contains two different magnetic atoms. In view of the isotypism with the strontium and barium compound, we expect divalent Eu. We have first investigated EuYb[Si_4N_7] by ^{151}Eu Mössbauer spectroscopy. The spectra at 296 and 78 K are presented in Figure 5 together with transmission integral fits. Both spectra could perfectly be fit with a single europium site at isomer shifts of $-12.97(3)$ mm s^{-1} at 296 and $-12.83(3)$ mm s^{-1} at 78 K. The experimental line widths are 2.8(2) mm s^{-1} (296 K) and 2.6(1) mm s^{-1}. The line widths are slightly larger than usually observed in divalent europium compounds (around 2.3 mm s^{-1}). This is most likely due to an overlap of two very similar ^{151}Eu signals of the two crystallographically different europium positions. Due to the non-cubic site symmetry both signals are subject to quadrupole splitting of ΔE_Q = 5.4(10) mm s^{-1} (296 K) and 5.7(8) mm s^{-1} (78 K). No signal occurs around an isomer shift of 0 mm s^{-1}, indicating pure divalent europium in our sample.

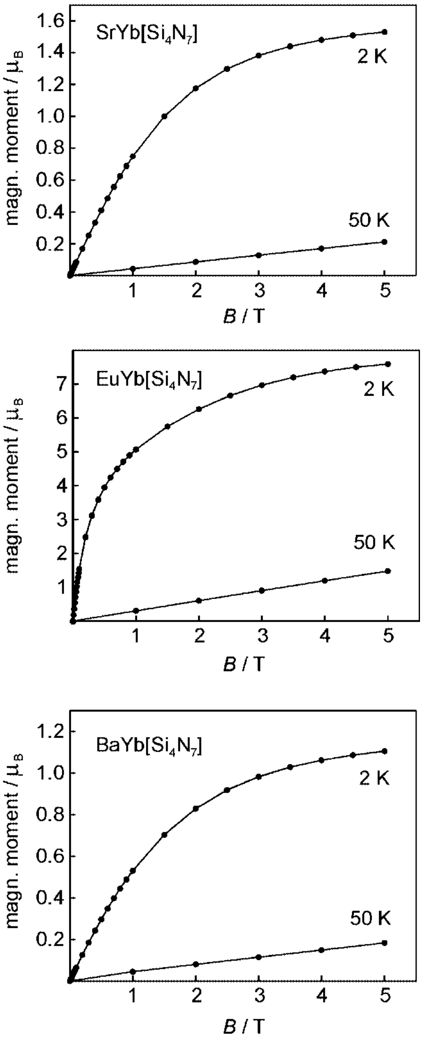

Fig. 4 Magnetization isotherms of SrYb[Si_4N_7], EuYb[Si_4N_7] and BaYb[Si_4N_7] at different temperatures.

The temperature dependent susceptibility data of EuYb[Si_4N_7] show nearly perfect Curie-Weiss behavior (Fig. 3) with the experimental values listed in Table 2. In the 3 T measurement we observe no *bump* around 70 K where EuO orders ferromagnetically [23–25]. Thus no EuO impurity is present in the sample of EuYb[Si_4N_7]. Assuming divalent Eu and trivalent Yb with free ion values of 7.94 μ_B/Eu^{2+} and 4.54 μ_B/Yb^{3+} one would expect a paramagnetic moment of 9.15 μ_B per formula unit EuYb[Si_4N_7] according to $\mu_{EuYb} = (\mu^2_{Eu} + \mu^2_{Yb})^{1/2}$. The experimentally determined value of 9.17 μ_B/f.u. is in good agreement with the theoretical value. Thus, in contrast to the strontium and the barium compound purely trivalent ytterbium occurs in EuYb[Si_4N_7]. There seems to be no oxygen content in the europium compound.

The magnetization behavior of EuYb[Si_4N_7] at 2 and 50 K is shown in Fig. 4. At 50 K we observe a linear increase similar to SrYb[Si_4N_7] and BaYb[Si_4N_7]. A steeper increase occurs at 2 K with a magnetization of 7.59(2) μ_B / f. u., slightly higher than the maximal possible value of

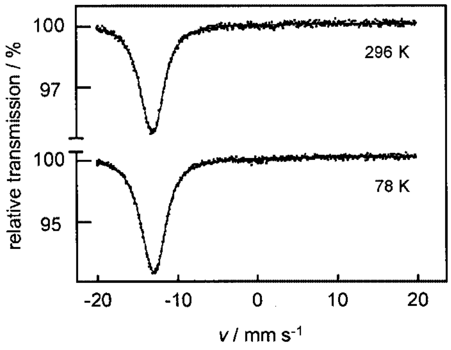

Fig. 5 Experimental and simulated ^{151}Eu Mössbauer spectra of EuYb[Si_4N_7] at different temperatures.

7 μ_B/Eu according to $g \cdot S$ [20]. The excess magnetic moment results from the ytterbium atoms. Most likely both the saturation moments of europium and ytterbium show a small reduction, probably due to crystal field effects.

The low temperature susceptibility data gave no hint for magnetic ordering of the three compounds down to 2 K. Also the measurement of the europium compound at 0.002 T in the temperature range $2 - 20$ K in zero-field and field-cooling mode gave no indication for magnetic ordering. The fitting parameters listed in Table 2 revealed slightly negative values for the Weiss constants. This might be indicative for antiferromagnetic interactions at temperatures below 2 K. The magnetization isotherms at 2 K, however, show an increase with increasing field strength. All the data give no hint for long-range magnetic ordering. We suppose that at 2 K the external field forces some of the magnetic moments from the paramagnetic state to a parallel spin alignment.

4 Conclusions

The ^{151}Eu Mössbauer spectroscopy revealed that Eu is divalent. Magnetic susceptibility measurements of MYb[Si_4N_7] (M = Sr, Ba, Eu) show paramagnetic behavior with experimental magnetic moments of 3.03(2), (Sr), 2.73(2) (Ba), and 9.17(2) (Eu) μ_B per formula unit. According to the non-magnetic character of the alkaline earth cations, Yb therefore has to be in an intermediate valence state Yb^{III-x}. Consequently, a partial exchange N^{3-}/O^{2-} resulting in compositions MYb^{III-x}[$Si_4N_{7-x}O_x$] with M = Sr, Ba or an introduction of anion defects according to MYb^{III-x}[$Si_4N_{7-x/3}\square_{x/3}$] with M = Sr, Ba have to be assumed, which presumably has been caused by a slight oxygen contamination of the alkaline earth metals used as starting materials. As the magnetic measurements gave no indication for intermediate valence Yb^{III-x} or mixed valent Yb^{II}/Yb^{III} in the europium compound the probable oxygen contamination might be ascribed to the alkaline earth metals. Even if very carefully purified these often contain significant amounts of oxygen. DFT calculations confirm both intermediate valency of Yb and the partial substitution of N^{3-} by O^{2-} on sites N1 and N2 [22]. The phase width x was estimated by comparing the theoretically expected magnetic moments of the respective compounds with the experimental magnetic moments and hence amounts to $0 \leq x \leq 0.4$. The maximum possible phase width is reached when all Yb atoms are divalent according to $x = 1$. In contrast to strontium and barium, in the europium compound the ytterbium atoms are in a stable trivalent state.

Acknowledgments. Financial support by the Fonds der Chemischen Industrie and especially by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. The authors thank *Prof. B. Winkler*, Institut für Kristallographie, Universität Frankfurt/Main, for valuable discussions.

References

[1] W. Schnick, H. Huppertz, *Chem. Eur. J.* **1997**, *3*, 679.
[2] W. Schnick, T. Schlieper, H. Huppertz, K. Köllisch, M. Orth, R. Bettenhausen, B. Schwarze, R. Lauterbach, *Phosphorus Sulfur* **1997**, *124/125*, 163.
[3] T. Schlieper, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1535.
[4] T. Schlieper, W. Schnick, *Z. Kristallogr.* **1996**, *211*, 254.
[5] M. Woike, W. Jeitschko, *Inorg. Chem.* **1995**, *34*, 5105.
[6] M. Woike, W. Jeitschko, *J. Solid State Chem.* **1997**, *129*, 312.
[7] K. Köllisch, H. A. Höppe, H. Huppertz, M. Orth, W. Schnick, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1371.
[8] H. A. Höppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, *J. Phys. Chem. Solids* **2000**, *61*, 2001.
[9] M. Orth, R.-D. Hoffmann, R. Pöttgen, W. Schnick, *Chem. Eur. J.* **2001**, *7*, 2791.
[10] H. A. Höppe, G. Kotzyba, R. Pöttgen, W. Schnick, *J. Mater. Chem.* **2001**, *11*, 3300.
[11] T. Schlieper, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1535.
[12] H. Huppertz, W. Schnick, *Acta Crystallogr.* **1997**, *C53*, 1751.
[13] H. A. Höppe, H. Trill, B. D. Mosel, H. Eckert, G. Kotzyba, R. Pöttgen, W. Schnick, *J. Phys. Chem. Solids* **2002**, *63*, 853.
[14] H. Huppertz, W. Schnick, *Angew. Chem.* **1996**, *108*, 2115; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1983.
[15] H. Huppertz, W. Schnick, *Z. Anorg. Allg. Chem.* **1997**, *623*, 212.
[16] H. Lange, G. Wötting, G. Winter, *Angew. Chem.* **1991**, *103*, 1606; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1579.
[17] T. Schlieper, W. Milius, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1380.
[18] W. Schnick, H. Huppertz, R. Lauterbach, *J. Mater. Chem.* **1999**, *9*, 289.
[19] R. B. von Dreele, A. C. Larson, *General Structure Analysis System*, Los Alamos National Laboratory Report LAUR 86-748, 1990.
[20] H. Lueken, *Magnetochemie*, Teubner, Stuttgart 1999.
[21] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York 1960, p. 543.
[22] B. Winkler, K. Knorr, W. Schnick, *unpublished.*
[23] B. T. Matthias, R. M. Bozorth, J. H. Van Vleck, *Phys. Rev. Letters* **1961**, *5*, 160.
[24] D. B. McWhan, P. C. Souers, G. Jura, *Phys. Rev.* **1966**, *143*, 385.
[25] B. Stroka, J. Wosnitza, E. Scheer, H. v. Löhneysen, W. Park, K. Fischer, *Z. Phys. B - Cond. Matter* **1992**, *89*, 39.