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A Europium-151 Mössbauer Spectral Study of $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$

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The europium-151 Mössbauer spectra of the $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ Zintl compounds, measured between 4.2 and 100 K, reveal europium(II) for all four crystallographically inequivalent europium sites in $Eu_{14}MnAs_{11}$ and $Eu_{14}MnSb_{11}$ and europium(II) and europium(III) for the three 32g and the 16f europium sites in $Eu_{14}MnP_{11}$, respectively. Below the ordering temperatures of 52, 74, and 92 K, only very small hyperfine fields of 2–4 T are observed at the europium sites as a result of the polarization by the manganese magnetic moments. At 4.2 K, the europium(II) magnetic moments are ordered, and hyperfine fields of 24.4, 24.8, and 19.3 T are observed in $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$, respectively, fields that are typical for magnetically ordered europium(II) ions. At 4.2 K the 16f europium(III) sites in $Eu_{14}MnP_{11}$ experience a transferred hyperfine field of 33 T from the neighboring ordered europium(II) moments. Between its Curie temperature and 4.2 K, the europium-151 Mössbauer spectra of $Eu_{14}MnSb_{11}$ reveal that the europium(II) moments order below ca. 13 K, i.e., below the second magnetic transition observed in magnetic measurements. Between their Curie temperatures and 4.2 K, the europium-151 Mössbauer spectra of $Eu_{14}MnP_{11}$ and $Eu_{14}MnAs_{11}$ are complex and have been analyzed with two models, models that give equivalently good fits. However, the second model in which the spectra are fit with a three-dimensional relaxation of the europium(II) and europium(III) hyperfine fields is preferred for its physical meaning and its reduced number of fitted parameters.

Introduction

The $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ Zintl compounds show[1−3] long-range ferromagnetic order below 52, 74, and 92 K, respectively. Because of the large distances of ca. 10 Å, the magnetic coupling between the manganese atoms cannot be explained by dipolar interactions and has been attributed[3−5] to a Ruderman−Kittel−Kasuya−Yosida (RKKY) exchange interaction[6,7] between the localized manganese moments via the conduction electrons. However, the magnetic behavior of these compounds is complex because the europium, when present as europium(II), also carries a magnetic moment.

The magnetic properties of $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ are summarized in Table 1. Specifically, $Eu_{14}MnP_{11}$ exhibits[2] ferromagnetic ordering below 52 K with

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Table 1. Crystallographic and Magnetic Properties[a]

parameter	$Eu_{14}MnP_{11}$	$Eu_{14}MnAs_{11}$	$Eu_{14}MnSb_{11}$
a, Å	15.930(4)	16.318(2)	17.326(7)
c, Å	21.213(5)	21.684(4)	22.75(3)
V, Å^3	5383(2)	5774(16)	6831(11)
V_{WS}, Å^3 Eu(1), 32g	37.427	38.438	41.163
V_{WS}, Å^3 Eu(2), 32g	39.132	40.550	44.303
V_{WS}, Å^3 Eu(3), 16f	34.401	35.630	38.782
V_{WS}, Å^3 Eu(4), 32g	38.457	39.709	43.311
θ, K[b]	57	72	93.55(3)
μ_{eff}^{so}, μ_B, calc	30.1	30.1	30.1
μ_{eff}, μ_B, obs[b]	28(1)	29.1(5)	27(1)
M_{sat}, μ_B, 5 K, calc[c]	102	102	102
M_{sat}, μ_B, 5 K, obs[a]	102.0(5)	95.0(5)	102.0(5)
T_c, K	52	74	92
T_t, K	−	25	15

[a] Data from refs 2 and 3. [b] The Weiss constant and effective paramagnetic moment obtained from the slope of the inverse magnetic susceptibility. [c] Calculated by assuming the presence of europium(II) and manganese(III) cations.

a saturation magnetization of 102 μ_B per formula unit, a magnetization that is expected if all the europium is divalent and the manganese is trivalent. Its observed effective moment, obtained from a modified Curie−Weiss fit, is 28(1) μ_B, a value that is slightly smaller than the 30.1 μ_B value expected for spin-only moments. $Eu_{14}MnAs_{11}$ shows[2] two magnetic transitions at 74 and 25 K. Its 5 K saturation magnetization is 95.0(5) μ_B per formula unit, a value that is lower than the expected 102 μ_B per formula unit. Finally, $Eu_{14}MnSb_{11}$ exhibits[1,3] ferromagnetic ordering below 92 K and a second magnetic transition at ca. 15 K, a temperature that decreases[1] with increasing applied field. The 5 K saturation magnetization is the expected 102 μ_B per formula unit, and the effective moment is 27(1) μ_B. Further, the maximum in the magnetization observed[2] at the second transition in $Eu_{14}MnAs_{11}$ and $Eu_{14}MnSb_{11}$ indicates that this ordering may be antiferromagnetic or canted ferromagnetic in nature.

The complex magnetic behavior of the $Eu_{14}MnPn_{11}$ compounds, where Pn is P, As, or Sb, results from the various magnetic exchange interations between the manganese and europium ions. A reasonable hierarchy of these exchange interactions, in decreasing magnitude, is Mn−Mn > Mn−Eu > Eu−Eu. Europium-151 Mössbauer spectroscopy is an excellent technique[8,9] for selectively probing the europium sublattice, determining its valence, and investigating its role in the magnetic behavior of complex solid-state materials. Further, in view of the difficulty in obtaining the magnetic structure of a europium-containing compound by neutron diffraction, europium-151 Mössbauer spectroscopy provides an alternative approach to obtaining insight into the magnetic structures of such compounds. In this paper, the results of a europium-151 Mössbauer spectral study of $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ are presented with the goal of investigating the Mn−Eu and Eu−Eu magnetic exchange interactions.

Experimental Section

The samples were freshly prepared as described[2,3] earlier and were protected from exposure to oxygen and moisture during their study. The europium-151 Mössbauer spectra were obtained on a constant-acceleration spectrometer that utilized a $^{151m}SmF_3$ source. The absorbers, which contained ca. 60 mg/cm^2 of powdered sample mixed with boron nitride, were prepared and maintained under a dry nitrogen atmosphere. The spectra were measured in a Janis Super-Varitemp cryostat, and the temperature was controlled with a Lakeshore Cryogenics temperature controller with an accuracy of at least 1% of the observed temperature. The velocity scale was calibrated at room temperature with a cobalt-57 source and α-iron foil. The isomer shifts are reported relative to EuF_3 at room temperature.

Europium-151 Mössbauer Spectral Results

$Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ crystallize[2,3] in the $I4_1/acd$ tetragonal space group with Z equal to 8; the lattice parameters are given in Table 1. In all three compounds there are four crystallographically distinct europium sites with Eu(1), Eu(2), and Eu(4) occupying the 32g general positions, with 16, 18, and 17 near neighbors, respectively, and with Eu(3) occupying the 16f special position with 14 near neighbors. Hence, in principle, four contributions, with relative areas 2:2:1:2, may be expected for the four sites in the europium-151 Mössbauer spectra of these compounds. These four europium sites differ both in their Wigner−Seitz cell volumes[10,11] (see Table 1) and in their corresponding near-neighbor environments, as given above. It is clear that in all three compounds the Eu(3) Wigner−Seitz cell volume is substantially smaller than that of the other three cell volumes.

A closer examination of the near-neighbor environment of each of the four europium sites in $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ indicates that Eu(1), Eu(2), and Eu(4) all have 10 europium near neighbors, whereas Eu(3) has only eight europium near neighbors. Further, only Eu(2) and Eu(4) have one manganese near neighbor. Finally, in $Eu_{14}MnP_{11}$, Eu(1) and Eu(2) have one Eu(3) among their 10 europium near neighbors, whereas Eu(4) has two Eu(3). As will be noted below, the Eu(3) is trivalent in $Eu_{14}MnP_{11}$.

Because the europium-151 Mössbauer spectra of $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ exhibit quite different behaviors as a function of temperature, the results and their discussion will begin with the simplest behavior, that of $Eu_{14}MnSb_{11}$, and continue with the more complex and unusual behaviors of $Eu_{14}MnAs_{11}$ and $Eu_{14}MnP_{11}$.

$Eu_{14}MnSb_{11}$. The europium-151 Mössbauer spectra of $Eu_{14}MnSb_{11}$, obtained between 4.2 and 100 K, are shown in Figure 1. The solid line is the result of a fit with one europium(II) component centered at −10 mm/s and one europium(III) component centered at 0.87 mm/s. The relative area of the europium(III) singlet absorption is 15% between 8 and 100 K and 10% at 4.2 K. This europium(III)

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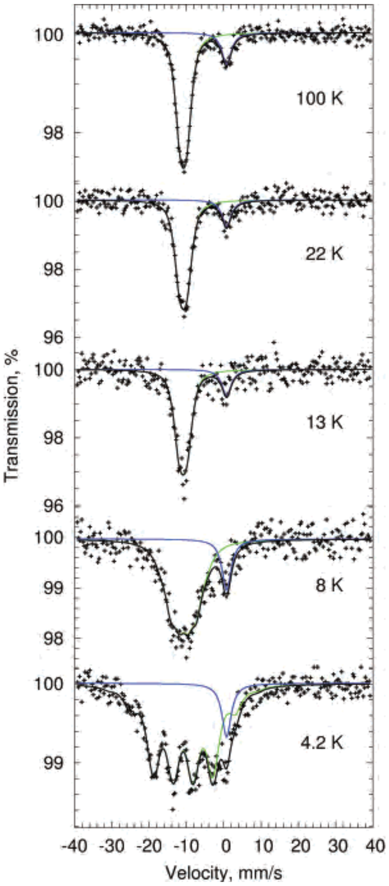

Figure 1. Europium-151 Mössbauer spectra of $Eu_{14}MnSb_{11}$ obtained at the indicated temperatures. The green and blue solid lines are the europium(II) and europium(III) components, respectively.

Table 2. Europium-151 Mössbauer Spectral Parameters for $Eu_{14}MnSb_{11}$

T, K	δ,[a] mm/s	H, T	area (% ϵ) (mm/s)
100	−10.80(3)	3.0(1)	19.2(4)
22	−10.82(5)	3.3(1)	23.4(6)
13	−10.89(8)	3.5(2)	23.3(7)
8	−10.74(13)	8.5[b]	30.3(7)
4.2	−10.87(7)	19.3(2)	31.6(6)

[a] The isomer shift is given relative to room-temperature EuF_3. [b] Parameter constrained to the value given.

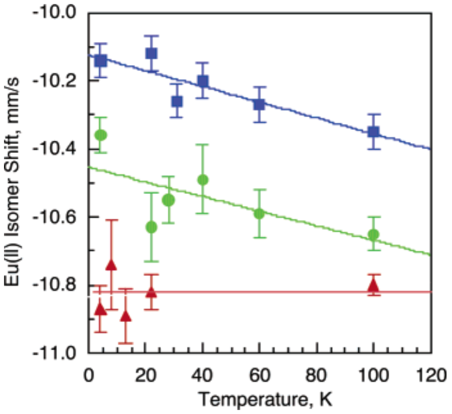

Figure 2. Temperature dependence of the Eu(II) isomer shift in $Eu_{14}MnP_{11}$ (blue squares), $Eu_{14}MnAs_{11}$ (green circles), and $Eu_{14}MnSb_{11}$ (red triangles). The straight lines are guides for the eye.

component is not believed to be intrinsic to the $Eu_{14}MnSb_{11}$ compound for three reasons. First, this singlet component may be fit with a line width of 3.0 ± 0.4 mm/s and an isomer shift of 0.77 ± 0.12 mm/s at all temperatures. This isomer shift is significantly smaller than that observed for the *intrinsic* europium(III) found in $Eu_{14}MnP_{11}$ (see below). Second, the narrow line width observed for this component both above and below the ordering transition of the europium(II) magnetic moments corresponds to a zero transferred hyperfine field, a field that is both expected and observed to be nonzero for the intrinsic europium(III) found in $Eu_{14}MnP_{11}$ (see below). Third, the 4.2 K Mössbauer spectrum (not shown) of an aged, and hence more oxidized, sample of $Eu_{14}MnSb_{11}$ exhibits a similar singlet component with the same isomer shift but a larger relative area. Hence, this singlet is assigned to an undefined europium(III)-containing impurity resulting from a minor oxidation of the sample. The europium(II) component has been fit as a magnetic component with zero quadrupole interaction at all temperatures. The resulting hyperfine fields and isomer shifts are given in Table 2.

The temperature dependence of the isomer shift observed for $Eu_{14}MnSb_{11}$ is shown in Figure 2. The isomer shift is typical of europium(II) and is, as expected,[8] virtually independent of temperature. At 100 K, above the Curie temperature of 92 K, the europium-151 Mössbauer spectrum is expected to show a zero magnetic hyperfine field unless, of course, there is some short-range order of the manganese magnetic moments slightly above the Curie temperature. Unfortunately, because of its intrinsically large line width, europium-151 Mössbauer spectroscopy is unable to distinguish the four different europium sites in the paramagnetic spectrum of $Eu_{14}MnSb_{11}$. At 100 K a fit with a single line with a line width of 3.9(1) mm/s is inadequate and indicates the need of several components. However, it seems essentially impossible to obtain a unique fit with four singlets assigned to the four europium sites in $Eu_{14}MnSb_{11}$. Thus, to compare the 100 K spectrum with the 22 and 13 K spectra (see Figure 1), spectra which also do not show any obvious hyperfine fields, the 100 K spectrum has been fit with a small field of 3 T. This field is an artifact of the fitting model and has been used both for comparison with the 22 and 13 K spectra and to mimic any distribution in the isomer shifts that results from the four crystallographically distinct europium(II) sites in $Eu_{14}MnSb_{11}$ (see above). At 22 K, i.e., well below the Curie temperature of 92 K, the "so-called" hyperfine field has increased to only 3.3 T, and hence, the ferromagnetic ordering of the manganese magnetic moments through the RKKY interaction and the polarization of the conduction electrons does not yield a significant hyperfine field at the europium(II) sites. It should be noted that only the Eu(2) and Eu(4) sites have manganese near neighbors, which could contribute to the field. At 13 K, below the second magnetic transition observed at 15 K (see Table 1), the 3.5 T hyperfine field is still very small, but at 8 and 4.2 K it has increased substantially as a result of the ordering of the europium(II) magnetic moments.

Unfortunately, europium-151 Mössbauer spectra cannot differentiate between ferromagnetic and antiferromagnetic

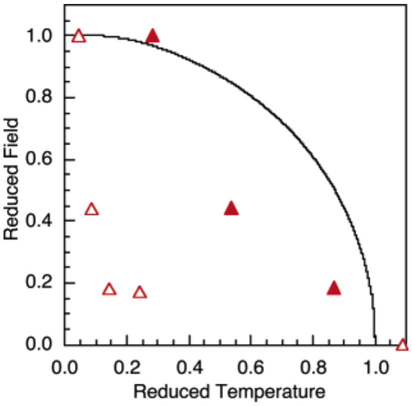

Figure 3. Reduced field in $Eu_{14}MnSb_{11}$ as a function of reduced temperature calculated with a critical temperature of 15 K (solid red triangles) and with a critical temperature of 92 K (open red triangles). The solid line is the Brillouin curve for $S = 7/2$.

ordering; a canted ferromagnetic state has been proposed[1] for $Eu_{14}MnSb_{11}$ at temperatures below 15 K. The temperature dependence of the hyperfine field observed for $Eu_{14}MnSb_{11}$ does not follow a Brillouin curve for spin 7/2, as would be expected[12,13] for europium(II), whether an ordering temperature of 92 or 15 K is used (see Figure 3). Rather, the hyperfine field decreases much more rapidly with increasing temperature. The non-Brillouin behavior of the hyperfine field in the three compounds will be commented upon in the discussion section. The 4.2 K hyperfine field of ca. 19 T observed in $Eu_{14}MnSb_{11}$ is substantially reduced from the Fermi contact field[8] of 34 T and is smaller than the hyperfine fields usually measured[12−14] in europium(II) compounds. A discussion of the hyperfine fields in the three compounds is presented below.

$Eu_{14}MnAs_{11}$. The europium-151 Mössbauer spectra of $Eu_{14}MnAs_{11}$, obtained between 4.2 and 100 K, are shown in Figure 4 (left). The spectrum obtained at 100 K has been fit with one europium(II) component with an isomer shift of ca. −10 mm/s. At 100 K, i.e., well above the Curie temperature of 74 K, no magnetic hyperfine field is expected or observed in the spectrum. Fits with a singlet with a line width of 5.6(2) and 5.2(2) at 60 and 100 K, respectively, have been obtained and indicate the more complex nature of the spectra. For the purpose of comparison with the spectra obtained at lower temperatures, the 100 K spectrum has been fit with a small hyperfine field of 3.5 ± 0.2 T and a line width of 3.4 ± 0.2 mm/s. As noted above for $Eu_{14}MnSb_{11}$, this field mimics the distribution of isomer shifts resulting from the four crystallographically different europium sites present in $Eu_{14}MnAs_{11}$. At 60 K, i.e., at a reduced temperature of 0.8 relative to the Curie temperature of 74 K, the europium(II) component is well fit with a hyperfine field of 4.1 ± 0.2 T and a line width of 3.4 ± 0.2 mm/s. This small hyperfine field results from the polarization of the europium(II) ionsthrough exchange with the ferromagnetically ordered manganese magnetic moments.

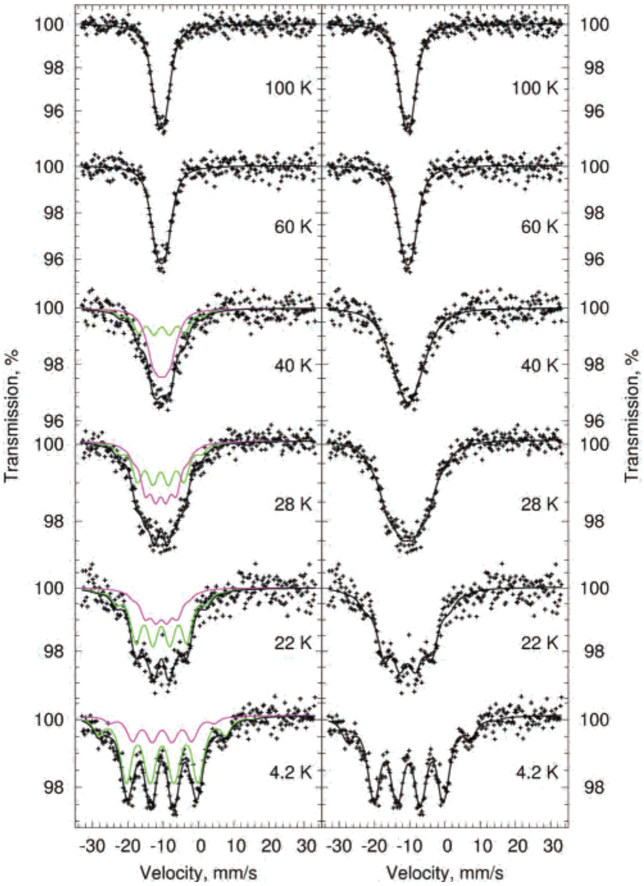

Figure 4. Europium-151 Mössbauer spectra of $Eu_{14}MnAs_{11}$ obtained at the indicated temperatures for model 1 (left) and model 2 (right). The green and magenta solid lines are the two europium(II) components.

Between 40 and 22 K, it is not possible to fit the $Eu_{14}MnAs_{11}$ spectra with a single magnetically split spectral component. Rather, two fitting models, 1 and 2, which give equally good misfits and χ^2 values that are close to 1, have been applied.

In model 1, two magnetically split components with the same isomer shift and line width and with different hyperfine fields and relative areas have been used; the total number of adjustable parameters is seven. Between 100 and 28 K, the line width was fixed at 3.2 mm/s, whereas, at 22 and 4.2 K, unconstrained fits yielded line widths of 3.3(3) and 3.2(2) mm/s, respectively. The resulting spectral fits are shown in Figure 4 (left panel), and the spectral parameters are given on the left of Table 3. The temperature dependence of the hyperfine fields and relative areas are shown in parts a and b of Figure 5, respectively. The existence of two europium(II) components with different hyperfine fields and relative areas, both of which are temperature dependent, is difficult to reconcile with the existence of four europium sites. Neither field shows the Brillouin dependence expected for a spin 7/2 europium(II) ion (see Figure 5c). We believe that model 1 is mathematically satisfactory but has no clear physical meaning.

In view of the rather apparent structure in the fitted solid line at 40 and 28 K (see Figure 4, left panel), the rather large

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Table 3. Europium-151 Mössbauer Spectral Parameters in $Eu_{14}MnAs_{11}$

	model 1				model 2		
T, K	*δ*, mm/s[a]	H_1, T	H_2, T	A_2	*δ*, mm/s[a]	*H*, T	*f*, MHz
100	−10.66(5)	–	3.8(1)	1[b]	−10.65(5)	3.37(3)	0[b]
60	−10.57(7)	–	4.4(2)	1[b]	−10.59(7)	3.98(3)	0[b]
40	−10.50(10)	15.9(6)	6.3(4)	0.59(5)	−10.49(10)	11.88(3)	68.4
28	−10.78(7)	16.0(4)	10.7(3)	0.53(5)	−10.55(7)	14.50(3)	27.6
22	−10.60(10)	17.6(3)	11.1(8)	0.32(6)	−10.63(10)	16.51(3)	11.6
4.2	−10.40(5)	24.8(3)	20.4(9)	0.27(8)	−10.36(5)	23.93(3)	0[b]

[a] The isomer shift is given relative to room-temperature EuF_3. [b] Parameter constrained to the value given.

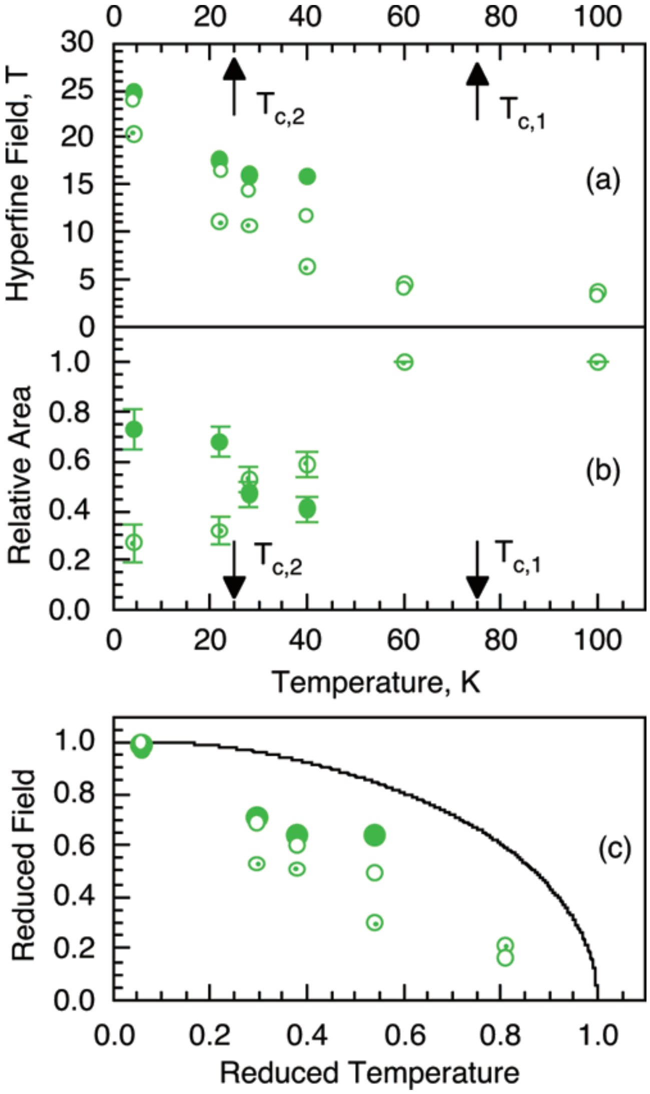

Figure 5. Temperature dependence of the hyperfine field (a) and relative area (b) in the Mössbauer spectra of $Eu_{14}MnAs_{11}$ obtained with model 1 (green solid and dotted circles) and model 2 (green open circles). (c) The reduced field as a function of the reduced temperature in $Eu_{14}MnAs_{11}$. The solid line is the Brillouin curve for S = 7/2.

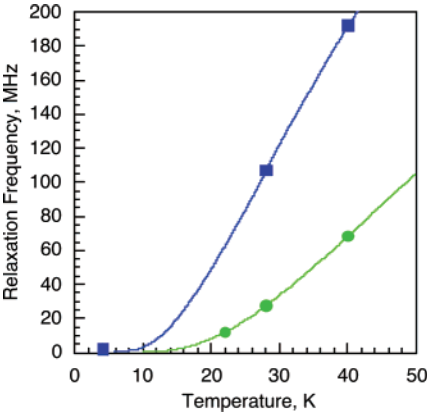

Figure 6. Temperature dependence of the relaxation frequency in $Eu_{14}MnP_{11}$ (blue squares) and in $Eu_{14}MnAs_{11}$ (green circles).

number of seven fitted parameters, and the lack of physical meaning of model 1, one may ask whether a relaxation model would not be more adequate to fit the observed spectra. Further, the presence of dynamic processes have already been observed[12−14] in the Mössbauer spectra of several related europium(II)-containing pnictide compounds. Hence, the Mössbauer spectra of $Eu_{14}MnAs_{11}$, obtained between 40 and 4.2 K, have been fit with model 2, a model that assumes[15,16] an isotropic relaxation of the hyperfine field in the random phase approximation. The total number of adjustable parameters is five in model 2, and the line width was constrained to 3.6 mm/s at all temperatures in order to allow comparison of the relaxation frequencies. The resulting fits are shown in Figure 4 (right panel), and the resulting spectral parameters are given on the right of Table 3. The temperature dependence of the isomer shift and of the hyperfine field is shown in Figures 2 and 5a, respectively. The temperature dependence of the isomer shift is in complete agreement with that observed for model 1. Further, the resulting hyperfine field is a value between the two hyperfine fields obtained in model 1, and its temperature dependence does not follow the Brillouin curve expected for a spin 7/2 europium(II) ion (see Figure 5c). The temperature dependence of the relaxation rate (see Figure 6) follows the typical Arrhenius thermal activation law with $f = f_0 \exp(-\Delta E/kT)$; the resulting activation energy is 85 K or 0.710 kJ/mol. Unfortunately, at this time there is no statistical basis for choosing between models 1 and 2 in the analysis of the europium-151 Mössbauer spectra of $Eu_{14}MnAs_{11}$, but model 2 has more physical meaning and also fits the Mössbauer spectra of $Eu_{14}MnP_{11}$, as is shown in the next section.

$Eu_{14}MnP_{11}$. The europium-151 Mössbauer spectra of $Eu_{14}MnP_{11}$, obtained at 100 and 60 K, show two absorption peaks at ca. −10 and 1.0 mm/s, assigned to europium(II) and europium(III), respectively. Initially they were fit with two single lines yielding line widths at 100 and 60 K, respectively, of 5.1(1) and 5.7(3) mm/s at ca. −10 mm/s and line widths of 2.59(1) and 2.47(2) mm/s at ca. 1 mm/s. The fits are satisfactory, but the large europium(II) line widths indicate the inadequacy of this simple model. An approach similar to that used for $Eu_{14}MnAs_{11}$ and $Eu_{14}MnSb_{11}$ is preferred and is used herein. The europium-151 Mössbauer spectra of $Eu_{14}MnP_{11}$, obtained at 100, 60, 22, and 4.2 K (see Figure 7, left panel, and Table 4), have been fit, in model 1, with one europium(II) component with an isomer shift of ca. −10 mm/s and one europium(III) component with an isomer shift of ca. 1.0 mm/s. In contrast,

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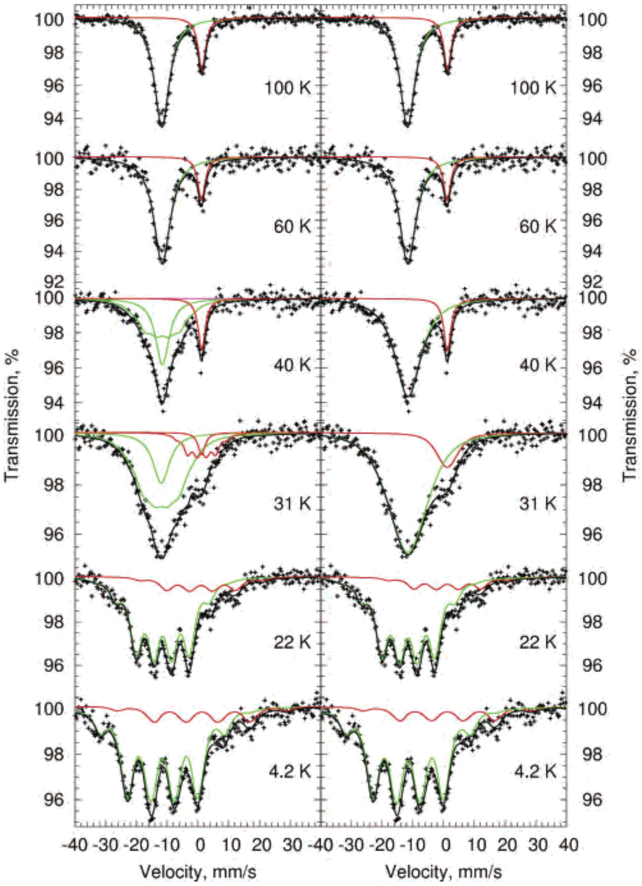

Figure 7. Europium-151 Mössbauer spectra of $Eu_{14}MnP_{11}$ obtained at the indicated temperatures for model 1 (left) and model 2 (right). The green and red solid lines are the europium(II) and europium(III) components, respectively.

Table 4. Europium-151 Mössbauer Spectral Parameters in $Eu_{14}MnP_{11}$, Model 1

T, K	δ_{II}, mm/s[a]	H_{II}, T	Γ_{II}, mm/s	p_{II}	δ_{III}, mm/s[a]	H_{III}, T	Γ_{III}, mm/s	p_{III}	A_{III}
100	−10.35	2.8	5.10	1[b]	1.02	–	2.59	1[b]	0.19
60	−10.27	2.8	5.67	1[b]	0.93	–	2.47	1[b]	0.15
40	−10.21	12.1	4.69	0.4	1.00	–	2.40	1[b]	0.14
31	−10.62	12.4	5.68	0.23	0.96	9.7	2.40	0.21	0.17
22	−10.13	18.3	3.66	0[b]	0.80	23.8	4.13	0[b]	0.18
4.2	−10.15	24.4	3.75	0[b]	1.07	33.2	3.70	0[b]	0.16

[a] The isomer shift is given relative to room-temperature EuF_3. [b] Parameter constrained to the value given.

the spectrum obtained at 40 K was fit with two europium(II) and one europium(III) components, and the spectrum obtained at 31 K was fit with two europium(II) and two europium(III) components, where the two europium(II) and the two europium(III) components each have the same isomer shift. The europium(III) component in $Eu_{14}MnP_{11}$ has a relative area of 17 ± 3% and the europium(III) observed in the 60 and 100 K spectra could a priori be assigned to an impurity resulting from oxidation of the sample as is the case (see above) for $Eu_{14}MnSb_{11}$, albeit a europium(III) component with a significantly different isomer shift. However, the spectra obtained at 4.2, 22, and 31 K can only be analyzed if a *magnetic* europium(III) component, with a relative area of 16 ± 2%, is included in the fit. But, there is *no plausible* europium(III) impurity compound that is known to order at low temperature or near the temperature at which $Eu_{14}MnP_{11}$ orders. In contrast, europium(III) in an ordered magnetic compound may exhibit a substantial hyperfine field, as has been revealed by the europium-151 Mössbauer spectrum[8,17] of europium iron garnet, $Eu_3Fe_5O_{12}$. Hence, we believe that the observed europium(III) component is intrinsic to $Eu_{14}MnP_{11}$. To support this conclusion, additional magnetic hysteresis measurements were made on several samples. In all cases, the saturation moments obtained were between 93 and 95 μ_B, lower than the previously reported value of 102 μ_B. If two of the 14 europium ions in $Eu_{14}MnP_{11}$ are present as europium(III) ions, the expected relative spectral area of the europium(III) component is 14.3%, if one assumes that the europium(II) and europium(III) recoil free fractions are the same. If, as is usually observed,[18] the europium(III) recoil free fraction decreases slightly more slowly than the europium(II) recoil free fraction with increasing temperature, the observed europium(III) relative area will be larger than 14.3%. Thus, we conclude that the Eu(3) ions, that occupy the 16f site, are present as europium(III) ions. In the structure of $Eu_{14}MnP_{11}$, the europium 16f site has the smallest Wigner−Seitz cell volume of the four europium sites in all three compounds (see Table 1) and hence is more likely to accommodate the smaller europium(III) ion than are the other three europium 32g sites. This conclusion is further supported by the preferential 16f site occupancy[19] exhibited by calcium(II), a cation that has an ionic radius similar to that of europium(III) in $Eu_{14-x}Ca_xMnSb_{11}$. Finally, the 4.2 K Mössbauer spectrum (not shown) of an aged sample of $Eu_{14}MnP_{11}$ showed a singlet centered at ca. 0 mm/s, similar to that observed in $Eu_{14}MnSb_{11}$ and characteristic of sample oxidation.

In model 1, the europium(II) and europium(III) isomer shifts in $Eu_{14}MnP_{11}$ are typical of these ions and are virtually temperature independent (see Table 4). The temperature dependence of the europium(II) and europium(III) hyperfine fields is shown in Figure 8a. Similarly to both $Eu_{14}MnAs_{11}$ and $Eu_{14}MnSb_{11}$, the europium(II) hyperfine field in $Eu_{14}MnP_{11}$ does not follow a Brillouin curve for a spin 7/2 europium(II) ion (see Figure 8b).

The coexistence of both a magnetically ordered and a paramagnetic europium(II) component as well as a paramagnetic europium(III) component, with paramagnetic fractions, p_{II} and p_{III}, respectively, at 31 and 40 K, is unexpected and difficult to rationalize in view of the magnetic data. In addition, in model 1, the number of fitted parameters, 10, is large and the europium(II) line widths are large between 31 and 100 K. Finally, the 40 and 31 K spectra of $Eu_{14}MnP_{11}$ exhibit a line shape profile that is similar to that of the 40 and 28 K spectra of $Eu_{14}MnAs_{11}$, spectra which are well fit with a relaxation model. Hence, the Mössbauer spectra of $Eu_{14}MnP_{11}$ between 4.2 and 40 K have been fit with the same random phase approximation relaxation of the hyperfine field.

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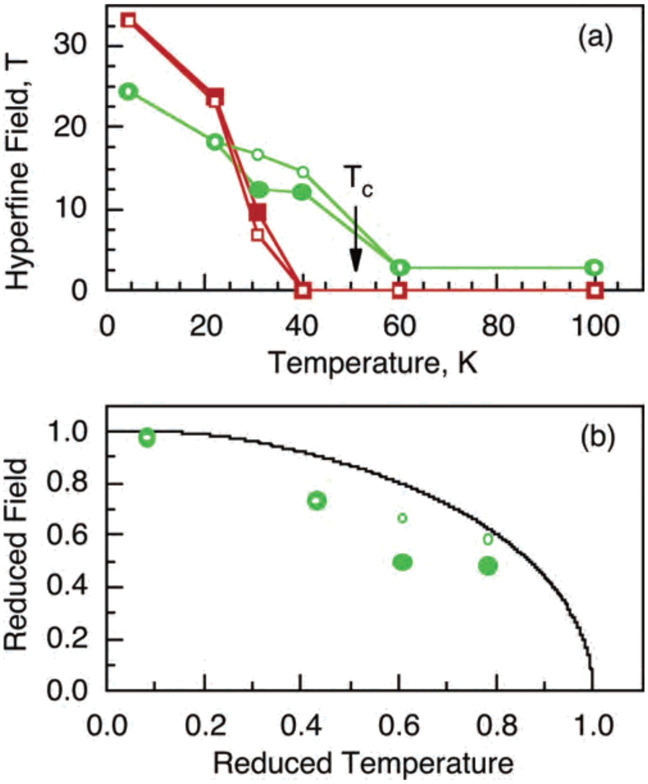

Figure 8. Temperature dependence of the hyperfine field (a) for the europium(II) (green circles) and europium(III) (red squares) in $Eu_{14}MnP_{11}$ obtained in model 1 (solid symbols) and model 2 (smaller open symbols). (b) The reduced europium(II) fields as a function of the reduced temperature in $Eu_{14}MnP_{11}$. The solid line is the Brillouin curve for $S = 7/2$.

Table 5. Europium-151 Mössbauer Spectral Parameters for $Eu_{14}MnP_{11}$, Model 2

T, K	δ_{II}, mm/s[a]	H_{II}, T	f_{II}, MHz	δ_{III}, mm/s[a]	H_{III}, T	f_{III}, MHz
40	−10.20	14.6	192	1.00[b]	0[b]	0[b]
31	−10.26	16.6	107	1.00[b]	6.9	42.9
22	−10.12	18.3	0.5	1.00[b]	23.1	0
4.2	−10.14	24.4	2.1	1.00[b]	33.0	0

[a] The isomer shift is given relative to room-temperature EuF_3. [b] Parameter constrained to the value given.

In this model 2, two relaxation profiles were fit, one for the europium(II) component and one for the europium(III) component. The relative area and isomer shift of the europium(III) component were fixed to 14% and 1.0 mm/s, respectively. The line width of the europium(II) and europium(III) components was fixed at 3.6 mm/s and the number of adjusted parameters is six. The results of the fits with model 2 are shown in Figure 7 (right panel), and the resulting spectral parameters are given in Table 5. The temperature dependence of the europium(II) isomer shift and hyperfine fields is shown in Figures 2 and 8a, respectively. As already noted for $Eu_{14}MnAs_{11}$ and $Eu_{14}MnSb_{11}$, the hyperfine field does not follow the Brillouin curve expected for a spin 7/2 europium(II) ion (see Figure 8b). The relaxation frequency, f_{II}, of the europium(II) field increases with increasing temperature with an Arrhenius thermal activation energy of 55 K or 0.455 kJ/mol (see Figure 6). The goodness of the fit parameter for model 1 and 2 fits shown in both panels of Figure 7 is equivalent, and it is impossible to choose between the two models on the basis of the quality of the fit. However, model 2 is preferred because of its physical meaning and its consistency with $Eu_{14}MnAs_{11}$.

At 4.2 K the europium(III) hyperfine field of 33 T observed in $Eu_{14}MnP_{11}$ is substantial. For comparison, 63 and 57 T fields are observed[17] in the europium iron garnet, fields that are transferred fields arising from the neighboring iron magnetic moments. In $EuFe_4Al_8$ at 4.2 K a smaller transferred[20] field of 14.8 T is observed at europium(III), a field that results from the ordered iron magnetic moments. In $Eu_{14}MnP_{11}$ the europium(III) transferred field results from only the eight europium(II) near-neighbor magnetic moments at distances of between 3.58 and 3.82 Å, moments that show at least partial magnetic ordering at 40 K. There are very few cases in the literature where the europium(III) transferred field results only from the europium(II) near-neighbor magnetic moments. In Eu_4As_3, which has a Curie temperature of ca. 20 K, the europium(II) and europium(III) hyperfine fields[21] are 24 and 23 T, respectively, and in Eu_3S_4, which has a Curie temperature of 3.2 K, the europium(III) hyperfine field[22] is only 5 T. Hence, it seems that the europium(III) hyperfine field increases with the ordering temperature of the europium(II) magnetic moments.

Discussion

The presence of europium(III) ions in $Eu_{14}MnP_{11}$ is rather unexpected. However, of the three compounds under study herein, $Eu_{14}MnP_{11}$ has the smallest unit-cell volume and hence is most likely to accommodate the smaller europium(III) ion. Further, the effective moment of 28 μ_B is smaller than the expected values of 30 μ_B calculated on the basis of europium(II) spin-only moments, and more recent hysteresis measurements indicate a lower saturation moment, approximately 95.0(5) μ_B. Hence, the magnetic data supports the presence of some europium(III) in $Eu_{14}MnP_{11}$. In contrast, in both $Eu_{14}MnAs_{11}$ and $Eu_{14}MnSb_{11}$ all the europium is divalent. It may seem surprising that the crystallographic structure of the $Eu_{14}MnPn_{11}$ compounds is able to accommodate both europium(II) and europium(III) ions without drastic changes, except for a small contraction of the lattice parameters in $Eu_{14}MnP_{11}$. However, it is known that in $Yb_{14}ZnSb_{11}$, ytterbium is present[23] as both ytterbium(II) and ytterbium(III). In this case, the intermediate valence apparently accounts for the charge discrepancy of zinc(II). If the model developed[24] for $Yb_{14}ZnSb_{11}$ is extended to $Eu_{14}MnP_{11}$, the compound that is the most semiconducting of the series, then manganese is divalent and there is an electron hole on the phosphorus, leading to a situation that is similar to the zinc(II) case in $Yb_{14}ZnSb_{11}$, and some of the europium ions become trivalent in order to retain charge balance.

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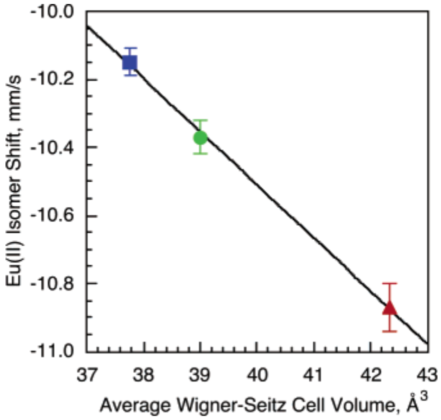

Figure 9. Correlation between the 4.2 K europium(II) isomer shift and the average Wigner−Seitz cell volume in $Eu_{14}MnP_{11}$ (blue square), $Eu_{14}MnAs_{11}$ (green circle), and $Eu_{14}MnSb_{11}$ (red triangle).

Unfortunately, the intrinsic resolution[7] of europium-151 Mössbauer spectroscopy does not permit the resolution of the four crystallographically inequivalent europium(II) sites. As is shown in Figure 2, the europium(II) isomer shift is the most negative in $Eu_{14}MnSb_{11}$ and the least negative in $Eu_{14}MnP_{11}$ as a result of the decrease in unit-cell volume. This volume effect on the isomer shift is better illustrated in Figure 9, which shows the correlation between the 4.2 K europium(II) isomer shift and the average Wigner−Seitz cell volumes of $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$. The least-squares fit straight line has a slope of −0.156 (mm/s)/Å^3. The negative slope indicates that the 6s electron density at the nucleus decreases upon going from $Eu_{14}MnP_{11}$ to $Eu_{14}MnSb_{11}$, in agreement with the influence[14,25] of an additional 6s electron on the isomer shift. Further, for a difference of 0.5 Å^3 in Wigner−Seitz cell volume between the four europium sites in $Eu_{14}MnPn_{11}$, a difference of only 0.078 mm/s in isomer shift is expected. Such a small difference is unobservable with the experimental europium-151 Mössbauer spectral line width of ca. 2.3 mm/s.

Before discussing the europium(II) hyperfine fields and their temperature dependence, it is worthwhile to note that there are three different magnetic exchange interactions in the $Eu_{14}MnPn_{11}$ compounds, interactions that decrease in magnitude in the order Mn−Mn > Mn−Eu > Eu−Eu. The Mn−Mn interaction occurs through the conduction electrons. In the crystallographic structure of the $Eu_{14}MnPn_{11}$ compounds, only two crystallographic sites, Eu(2) and Eu(4), have one manganese near neighbor. Hence, the polarization of the europium(II) through a direct Mn−Eu interaction must be small. The distribution of the electric charges within the lattice of the $Eu_{14}MnPn_{11}$ compounds is also more complex than simply divalent europium and trivalent manganese. Antimony M_{45}-edge XMCD measurements[26] and ab initio calculations[24] of the electronic band structure of Yb_4MnSb_{11} and of the analogous $A_{14}MnBi_{11}$ compounds have already shown both that manganese is divalent in the $MnSb_4$ tetrahedral clusters present in the crystallographic structure and that the four antimony sites have an unpaired spin that is antiparallel to the manganese moment and may be associated with the Sb_4 5p electrons. Unfortunately, the variety of magnetic exchange interactions and the complexity of the electronic structure of the $Eu_{14}MnPn_{11}$ compounds make it difficult to provide a highly detailed discussion of the europium hyperfine fields and their temperature dependence.

In metallic compounds the hyperfine field at europium consists of three contributions:[8] the core-polarization field, H_{core}; the conduction electron polarization by the ion itself, H_{cond}; and all contributions from neighboring magnetic ions, H_n. H_{core} is equal to −34 T. H_{cond} results from the orbital polarization of the 6s and 5d conduction electrons by the 4f europium magnetic moment and is usually on the order of 10 T. H_n results from the contributions of the neighboring magnetic moments and its absolute value of ca. 5 T is usually less than that of H_{cond}, but its sign depends on the orientation of the neighboring magnetic moments. In the case of $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$, the europium and manganese neighbors of a given europium site are found at rather large distances of 3.4−4.6 Å and their contribution to H_n is thus likely to be small. The small hyperfine fields of at most 3.5−4 T but more likely of 0.5−1 T obtained upon cooling to a temperature of one-half the Curie temperature indicate that the contribution from the manganese magnetic moments is small. Hence, the ca. 24 T absolute values of the 4.2 K fields measured in $Eu_{14}MnP_{11}$ and $Eu_{14}MnAs_{11}$ are very typical. The 4.2 K field of ca. 19 T in $Eu_{14}MnSb_{11}$ may not be fully saturated, as the ordering temperature of the europium(II) moments is only 15 K. Alternatively, it may result from a H_{cond} contribution that is larger than 10 T, probably because the antimony 5p electrons interact more effectively with the europium 5d electrons and, thus, contribute to a more effective polarization of the conduction electrons. The importance of the role of the antimony 5p electrons on the magnetic properties of Yb_4MnSb_{11} and Eu_4MnSb_{11} is currently under investigation[27] by ^{121}Sb Mössbauer spectroscopy.

In $Eu_{14}MnSb_{11}$, the magnetic transition at 92 K is clearly associated with the ordering of the manganese magnetic moments through an RKKY exchange interaction, whereas the transition at 15 K is associated with the ordering of the europium(II) magnetic moments. Unfortunately, the Mössbauer spectra cannot distinguish between ferro- and antiferromagnetic ordering. The Mössbauer spectra of $Eu_{14}MnP_{11}$ and $Eu_{14}MnAs_{11}$ are well fit with a relaxation model, as is shown in Figures 4 and 7 (right panels). The activation energies of the relaxation process are similar to the activation energies of 0.7 and 1.35 kJ/mol, which have been reported[14] for the relaxation process in LiEuSb and LiEuP, respectively. In this latter case, the relaxation process was attributed to spin fluctuations. However, the basis for this relaxation is unclear. The existence of the RKKY oscillatory nature or of spin waves may play an important role that cannot be

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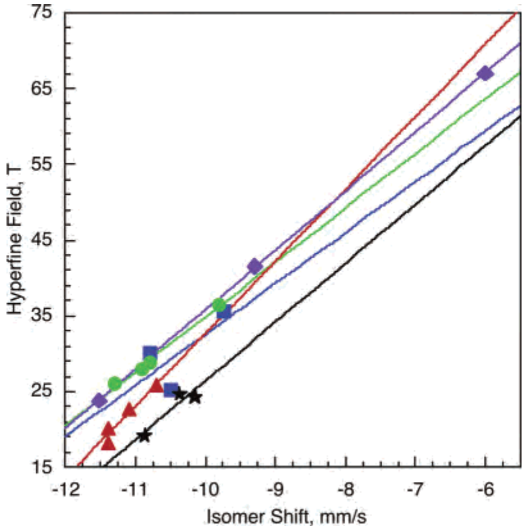

Figure 10. Saturation hyperfine field as a function of the isomer shift in EuM_2P_2 (blue squares) and EuM_2As_2 (green circles), where M is Fe, Co, Ni, or Pd; in LiEuPn (red triangles), where Pn is P, As, Sb, or Bi; in $EuFe_4P_{12}$, $EuRu_4P_{12}$, and $EuFe_4Sb_{12}$ (black diamonds); and in $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ (black stars).

investigated further. The Mössbauer spectra, in the framework of model 2, indicate that the europium(II) moments are relaxing isotropically and slowly on the Mössbauer time scale of 10 ns. In the magnetic measurements, there is an applied field, and the europium(II) moments are static in this field. Hence, Mössbauer spectra in the presence of an applied field may yield a choice between models 1 and 2. The absence of relaxation in the Mössbauer spectra of $Eu_{14}MnSb_{11}$ may result from the lower ordering temperature of the europium(II) magnetic moments.

In none of the three compounds does the hyperfine field follow a Brillouin 7/2 curve, as would be expected for ordered europium(II) magnetic moments. A less obvious non-Brillouin behavior of the hyperfine field has already been observed[14] in the LiEuPn compounds and assigned to spin fluctuations, fluctuations which are disregarded in the Weiss molecular field model that associates an effective field with an average spin. In contrast to the LiEuPn compounds, which contain only one magnetic europium(II) ion, the $Eu_{14}MnPn_{11}$ compounds contain two magnetic ions and the hyperfine field measured at the europium(II) sites result from Mn−Eu and Eu−Eu exchange interactions. In addition, the valence[24] of the manganese ion is clearly not three. Hence, it is not possible to predict the temperature dependence of the hyperfine field on the basis of a simple molecular field theory for $S = 7/2$, as would be expected for europium(II).

Because the isomer shift and the hyperfine field are both functions of the electron densities in the 6s, 5d, and 4f valence orbitals, several authors[13,14,28,29] have extracted various linear relationships between these two hyperfine parameters. The "Wickman" and "Zinn" relationships[28,29] have already been found[13,14] to be inappropriate both for compounds with the $ThCr_2Si_2$ structure and for the LiEuPn pnictides. In Figure 10, the saturation hyperfine field is plotted as a function of the isomer shift in EuM_2P_2 and EuM_2As_2 (where M is Fe, Co, Ni, or Pd), in LiEuPn (where Pn is P, As, Sb, or Bi), in $EuFe_4P_{12}$, $EuRu_4P_{12}$, and $EuFe_4Sb_{12}$, and in $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$. There is a very good linear correlation between the saturation hyperfine field and the isomer shift for the four groups of compounds, except for the EuM_2P_2 group, where M is Fe, Co, or Pd. However, the sign of the slope of the straight lines in Figure 10 is contrary to expectation. Indeed, the 6s electron density at the europium nucleus decreases as the isomer shift becomes more negative, and hence, the contribution to the hyperfine field of the 6s electron polarization also decreases its positive value, and the effective hyperfine field should become more negative, i.e., its absolute value should increase contrary to the observation in Figure 10. Hence, if Figure 10 cannot be understood in terms of only the 6s electron contributions to the isomer shift and hyperfine field, the 5d electrons, which have a smaller influence[8] on the isomer shift, must influence[14] the hyperfine field through their polarization. It would be interesting to study the antimony-151 Mössbauer spectra of $Eu_{14}MnSb_{11}$ in order to investigate the presence of a transferred field on antimony, the presence of which would support the importance of the role of the 5d electrons.

In conclusion, $Eu_{14}MnP_{11}$, $Eu_{14}MnAs_{11}$, and $Eu_{14}MnSb_{11}$ each exhibit magnetic behavior that is both complex and different because of the presence of europium(III) ions in $Eu_{14}MnP_{11}$, the presence of relaxation of the europium(II) magnetic moments in $Eu_{14}MnP_{11}$ and $Eu_{14}MnAs_{11}$, and the ordering of the manganese and europium magnetic moments at very different temperatures in $Eu_{14}MnSb_{11}$.

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