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¹¹⁹Sn HYPERFINE FIELDS IN RMn_6Sn_6 (R = Mg, Zr, Hf). EXPERIMENTAL AND THEORETICAL STUDY

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We performed both ¹¹⁹Sn Mössbauer experiments and electronic structure calculations using the Korringa-Kohn-Rostoker method on the hexagonal RMn₆Sn₆ (R = Mg, Zr, and Hf) compounds. According to previous neutron diffraction results two types of commensurate magnetic order are investigated: ferromagnetic for R = Mg and antiferromagnetic for R = Zr and Hf. From ¹¹⁹Sn Mössbauer measurements, high transferred hyperfine fields on the tin nuclei are observed. The $H_{\rm hf}$ values are well supported by the Korringa-Kohn-Rostoker results. Moreover, the calculated $\mu_{\rm Mn}$ are in good agreement with the neutron diffraction data. When observing the density of states, ZrMn₆Sn₆ is found near semimetallic limit.

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1. Introduction

The hexagonal HfFe₆Ge₆-type RMn₆Sn₆ compounds (P6/mmn) involving non-magnetic R elements (R = Mg, Sc, Y, Zr, Hf, and Lu) are known to order magnetically above room temperature [1-4]. From neutron diffraction three different magnetic arrangements have been found: ferromagnetic (R= Mg), antiferromagnetic (high temperature phases (H.T.) of R = Zr, Hf, and Lu) and helimagnetic (R = Sc, Y and low temperature phases of R = Zr, Hf, Lu) with an Mn moment value of $\mu_{Mn} \approx 2.2 \ \mu_B$ at 2 K. Previously, the occurrence of large transferred hyperfine fields has been shown on inequivalent Sn sites in YMn₆Sn₆ [5].

In this paper, the magnetic properties of $MgMn_6Sn_6$, $ZrMn_6Sn_6$ (H.T.) and $HfMn_6Sn_6$ (H.T.) are studied by ¹¹⁹Sn Mössbauer spectroscopy and electronic structure calculations performed by the Korringa-Kohn-Rostoker (KKR) method within the local spin density approximation.

2. Crystal and magnetic structures

In the HfFe₆Ge₆-type RMn₆Sn₆ compounds the Mn atoms occupy the 6(i) (1/2, 0, $z_{\rm Mn} \approx 0.25$) site, the R atoms enter the 1(b) site (0, 0, 1/2) while the Sn atoms are located on three different sites, namely, Sn(2c) (1/3, 2/3, 0), Sn(2d)

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(1/3, 2/3, 1/2) and Sn(2e) $(0, 0, z_{Sn} \approx 0.17)$. The Sn(2c) and Sn(2d) atoms are situated in trigonal Mn prisms with three additional R atoms in the basal plane for Sn(2d). The Sn(2e) atom is slightly outside of the hexagonal Mn plane (Kagomé net) with one R atom and one Sn(2e) atom as next nearest neighbors along the *c*-axis.

MgMn₆Sn₆ is ferromagnetic below $T_{\rm C} = 290$ K, while the Zr and Hf-based compounds are antiferromagnetic below $T_{\rm N} = 580$ K and 575 K, respectively. The neutron diffraction studies have shown that their magnetic structures may be described as an alternative stacking (along the *c*-axis) of two different slabs built upon ferromagnetic easy-plane (001) Mn sheets: the ferromagnetic Mn-Sn(2e)-Sn(2c)-Sn(2e)-Mn slab, and the Mn-(R,Sn(2d))-Mn slab. Within this slab the Mn-Mn interlayer coupling has been found strongly dependent on both the R valency and temperature [4]. Then, for R = Mg the interlayer coupling is ferromagnetic, otherwise antiferromagnetic coupling occurs down to $T_{\rm t}$ (\approx 70 K for R = Zr and Hf) where non-collinear behavior takes place leading to incommensurate magnetic arrangements ($\mu_{\rm Mn} \approx 2.2 \,\mu_{\rm B}$ at 2 K in all cases). Note that no change in the magnitude of the ordered magnetic moment is observed at the commensurate-incommensurate transition.

3. ¹¹⁹Sn Mössbauer study

¹¹⁹Sn Mössbauer spectra were recorded from 4.2 K to room temperature and refined with the least-squares method as described in Ref. [6]. The hyperfine parameters are obtained with respect to BaSnO₃ at room temperature. In all cases, the ¹¹⁹Sn Mössbauer spectra (Fig. 1) are characteristic of tin nuclei experiencing large transferred $H_{\rm hf}$.

From the axial local symmetry at the three Sn sites one expects $\eta = 0$. Therefore, for a magnetic site the apparent quadrupolar splitting is given by

$$2\epsilon = \frac{eQV_{zz}}{2} \left(\frac{3\cos^2\Theta - 1}{2}\right) = \Delta_p \left(\frac{3\cos^2\Theta - 1}{2}\right),$$

while the appearance of a quadrupolar doublet (Fig. 1) on Sn(2d) for R = Zr and Hf



Fig. 1. ¹¹⁹Sn Mössbauer spectrum of HfMn₆Sn₆ at 100 K.

TABLE I

		Mg (4.2 K)	Zr (100 K)	Hf (100 K)
Sn(2e)	$2\epsilon \text{ (mm/s)}$	0.04	0.00	0.00
	$H_{\rm hf}~({ m kG})$	217	257	262
Sn(2d)	$2\epsilon \text{ (mm/s)}$	-0.68	$ \Delta_p = 1.05$	$ \Delta_p = 1.12$
	$H_{\rm hf}~({ m kG})$	325	0	0
Sn(2c)	$2\epsilon \; (mm/s)$	-1.00	-0.77	-0.80
	$H_{\rm hf}~(\rm kG)$	300	321	315

Hyperfine parameters in RMn_6Sn_6 (R = Mg, Zr and Hf) compounds.

above T_t well corresponds to the antiferromagnetic neighborhood around this site deduced from neutron diffraction experiments [4]. According to the point charge approximation, the values of the electric field gradient at the Sn sites are related to $|V_{zz}^{2e}| < |V_{zz}^{2d}| < |V_{zz}^{2c}|$. Since the easy-plane magnetization deduced from neutron diffraction involves $\Theta = 90^{\circ}$, the sites attribution becomes obvious (Table I). In each case the chemical isomer shift value is close to IS $\approx 2 \text{ mm} \cdot \text{s}^{-1}$ for the three tin sites.

4. KKR calculations

The electronic structure calculations are performed by the nonrelativistic self-consistent KKR method [7, 8] within the LSD approximation (using exchange-correlation term of von Barth-Hedin [9]). The calculations are carried out with the following a/c lattice parameters (in Å): 5.489/8.971, 5.451/8.972, and 5.431/8.950 for MgMn₆Sn₆, ZrMn₆Sn₆, and HfMn₆Sn₆, respectively. Similar radii of non-over-lapping muffin-tin spheres are chosen for the different atoms (identical for the inequivalent Sn sites), giving a filling factor of the Wigner-Seitz $\approx 60\%$. The hyperfine field at tin nuclei is calculated using the Fermi contact formula [10], which in the nonrelativistic limit is given by $H_{\rm hf} = \frac{8}{3}\pi\mu_{\rm B}^2 [\rho \uparrow (0) - \rho \downarrow (0)]$, where $\rho \uparrow (0)$ and $\rho \downarrow (0)$ denote the spin-dependent electron densities extrapolated to r = 0 [11]. Since the calculated magnetic properties refer to purely ferromagnetic (antiferromagnetic) ground state, the finite temperature $H_{\rm hf}$ values (Table I) obtained for R = Zr and Hf are extrapolated to T = 0 K and next compared in Table II.

As expected for tin atoms [12], the main contribution to the hyperfine field comes from valence electrons, then the $H_{\rm hf}$ sign, found in KKR, is the same as the

TABLE II

The calculated hyperfine fields on Sn (kG) and magnetic moments (μ_B) on Mn in RMn₆Sn₆. Experimental values are in parenthesis.

		R = Mg	R = Zr	R = Hf
$H_{\rm hf}$	(2e)	202(217)	229(265)	274(272)
	(2d)	338(325)	0(0)	0(0)
	(2c)	335(300)	378(331)	330(328)
μ_{Mn}		2.22(2.32)	2.19(2.11)	2.36(2.18)



Fig. 2. Total density of states for ZrMn₆Sn₆.

Sn local magnetic moment while opposite to magnetic moment on surrounding Mn atoms. The density of states of $ZrMn_6Sn_6$ is presented in Fig. 2, with a particular shape near the Fermi level, forecasting a semimetallic behavior.

5. Conclusion

Our study on RMn_6Sn_6 (with R = Mg, Zr, and Hf) shows the remarkable agreement between the experimental results and the KKR band structure computations with respect both to magnetic moments and transferred hyperfine fields. A more detailed presentation of the ¹¹⁹Sn Mössbauer study and the KKR electronic structure results will be published elsewhere.

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