

## Appearance potential study of $\text{PrMn}_2$ and $\text{SmMn}_2$ intermetallics

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### Abstract

Soft X-ray appearance potential spectroscopy (SXAPS) has been employed to study the changes in the electronic structure of  $\text{PrMn}_2$  and  $\text{SmMn}_2$  intermetallics as a result of alloying. In this technique the total X-ray emission associated with the thresholds for the excitations of core levels of the atoms in the surface region of the materials is measured. It sensitively provides information regarding the density of unoccupied states at the Fermi level. The SXAPS spectra of the  $M_{4,5}$  levels of Pr and Sm and the  $L_{2,3}$  levels of Mn in these intermetallics are compared with the corresponding elemental spectra. The observed shift in the core levels represents contribution from the shifts due to charge transfer and that due to the hybridization between the Mn 3d and the rare earth 5d bands. The charge transfer shifts have been estimated from the differences in the Fermi levels of the intermetallic and the element using the free electron model. These values have been utilized to obtain the hybridization shifts. The hybridization shifts show a decreasing trend in these intermetallics and is attributed to the decrease in the number of electrons in the 3d–5d hybridized bands. Our results correlating the Mn magnetic moment with the number of electrons are consistent with the reported experimental data. It is concluded that the 3d–5d hybridization plays a significant role in determining the magnetic properties of these intermetallics.

**Keywords:** Intermetallics; Electronic structure; SXAPS

### 1. Introduction

The rare earth (R) and manganese intermetallics of the type  $\text{RMn}_2$  exhibit a variety of magnetic properties depending upon the rare earth element [1–8]. To a large extent this is due to the competition between the localized R–4f electrons and the itinerant Mn–3d electrons which frequently leads to a complex magnetic behavior being visible in non collinear spin structures and spin reorientations [6–8]. The Mn moment is close to instability. Thus, the magnetic properties depend sensitively upon interatomic distances. Huge magnetovolume effects occur [9] which are supposed to be associated with a critical value of the Mn–Mn distance,  $d_c = 2.66 \text{ \AA}$  at ambient temperature, below which the Mn moment is unstable. This value happens to be present in  $\text{DyMn}_2$ . Consequently, in this and the following heavy rare earth compounds, there is only an induced moment present at the Mn site and the magnetic properties are dominated by the RKKY-interaction of the rare earth sublattice. For the light rare earths, large spontaneous moments of about  $2.7 \mu_B$  per Mn atom are present.

The 4f moments interact with the 3d moments via a 5d–3d hybridization. The importance of the R–5d Mn–3d coupling due to local exchange interactions was first considered by Campbell [10] and more recently corroborated by Brooks et al. [11–13] using band structure calculations. Duc [14,15] demonstrated for a large number of R–transition metal (T) compounds that the R–T exchange interaction can be well understood by applying this 3d–5d hybridization model. The electronic structure of  $\text{RMn}_2$  compounds is not yet completely understood. Its knowledge would help in explaining the complex magnetic properties of these compounds. The 3d–5d hybridization plays a critical role in producing significant 5d electron charge and spin density at the R sites and is responsible for the coupling between 5d and 3d spin directions and thus eventually for the 4f and 3d spin directions. The study of the hybridization of 3d and 5d bands is therefore of essential importance in elucidating the magnetic properties of these R–T intermetallics.

In the present investigation we have employed soft X-ray appearance potential spectroscopy (SXAPS) to study the conduction band density of states in the  $\text{RMn}_2$

compounds. In the SXAPS technique the derivative of the total X-ray fluorescence yield from the sample surface as a function of bombarding electron energy is measured. At the threshold of excitation of one of the core levels, both the incident and core electrons are excited to the Fermi level,  $E_F$  resulting in the appearance of an abrupt increase in the total X-ray intensity. The intensity of the soft X-ray emission is determined by the product of the atomic concentration  $n$  and the self-convolution

$$\int_0^E N(E')N(E-E') dE'$$

of the electronic density of unoccupied states,  $N(E)$  above  $E_F$  [16–18]. As the matrix element governing the core hole production involves a very short range wave function of the initial core electron state, the technique reveals a localized density of states (DOS). The details of the technique can be found elsewhere [17,19]. SXAPS is very sensitive to the DOS in the conduction band. Transition metals and rare earths have high unoccupied DOS at  $E_F$  making SXAPS a highly suitable technique to study the changes in the electronic configuration of these elements as a result of alloying. The SXAPS signal relates to the self-convolution of the one-electron DOS above  $E_F$ . This theory has worked quite well for the 3d transition metals where core level transitions to unoccupied conduction band states occur. In rare earths, the core electron is not excited to the conduction band but to unoccupied 4f orbitals which are quite localized about the excited ion. Therefore, the theory does not adequately explain the SXAPS signal obtained from rare earths.

In this investigation we report the SXAPS study on  $\text{PrMn}_2$  and  $\text{SmMn}_2$  intermetallics. The corresponding elemental spectra are also included for comparison. The observed experimental core level shift has been utilized to estimate the shifts due to hybridization of the Mn 3d and rare earth 5d bands. The data are compared with those on  $\text{GdMn}_2$  reported earlier [20]. The observed decrease in the shift due to hybridization is related to the decrease in the Mn magnetic moment in these intermetallics.

## 2. Experimental

In the SXAPS technique the sample is positively biased and electrons from a tungsten filament are incident on the sample. The accelerating voltage on the sample is linearly increased with a ramp generator. The soft X-rays produced are detected photoelectrically. When the target potential approaches the threshold for core level excitation of surface atoms, there is a sudden increase in the photoelectron current. The signal

is extracted from the Bremsstrahlung background by recording the data in the first differential mode. This is accomplished by the modulation technique using a phase-lock amplifier. The details of the technique have been described earlier [21]. The resolution of the spectrometer was 1.0 eV, although changes in the threshold energy could be determined with an accuracy of 0.1 eV.

The samples were prepared by induction melting the high purity (99.95%) starting materials. In order to avoid the formation of  $\text{R}_6\text{Mn}_{23}$  the stoichiometry 1:1.93 was chosen. The as-cast samples were annealed in a high vacuum at 760 °C for one week. X-ray diffraction and a.c. susceptibility measurements were used to check the phase purity. Both compounds were found to have crystallized in the hexagonal C14 Laves phase type. In this structure the R atoms are located on a diamond lattice, while the Mn atoms lie on corner sharing tetrahedra, exhibiting a stacking along chains in the  $c$ -direction. The samples were lightly sputtered in the analysis chamber by low energy argon ions and annealed. The contamination of the samples was checked by recording the oxygen and carbon K-level spectra. These spectra were barely observable, thus ensuring clean surfaces for examination. The system operating pressure was approximately  $10^{-9}$  Torr. The SXAPS spectra in the  $M_{4,5}$  core level region of Pr and Sm and the  $L_{2,3}$  regions in Mn were recorded in the intermetallics and in the pure elements. The spectra were recorded with an emission current of 5.0 mA. The modulation signal used had a frequency of 5.5 kHz and an amplitude of 1.0  $V_{p-p}$ .

## 3. Results and discussion

The SXAPS spectra shown in the figures discussed below are the plots of the first differential of the X-ray yield as a function of the sample potential. The spectra represent the average of several runs to improve the signal-to-noise ratio. The binding energy (BE) is the minimum energy required to excite the core electron to the lowest available unoccupied state above  $E_F$ . In this investigation the BE was determined by the point of intersection of an extrapolated base line and the low energy edge of the peak. The threshold energies of the peaks are corrected for the instrumental effects which, in the present investigation amount to 5.0 eV [22].

The 3d levels ( $M_{4,5}$  levels) of Pr in both the elemental and the compound are shown in Fig. 1. They are found to exhibit the spin-orbit doublet corresponding to the  $3d_{5/2}$  and  $3d_{3/2}$  levels. The splitting is observed to be 19.1 eV for both the pure element and the compound. Each level exhibits a structure consisting of an intense peak followed by an undershoot. This is characteristic

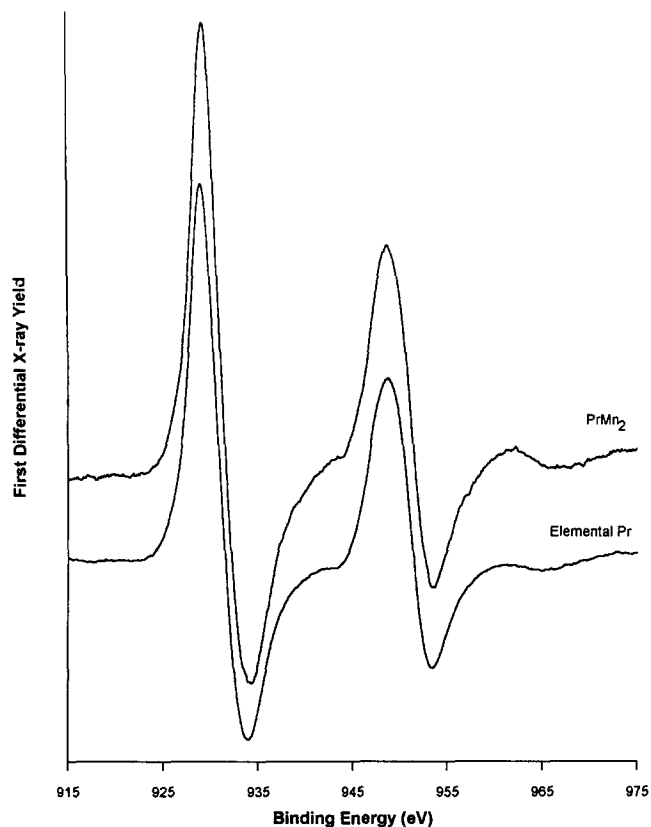


Fig. 1.  $M_{4,5}$  level SXAPS spectra of Pr in the elemental state and in the intermetallic  $\text{PrMn}_2$ . The spectra were recorded with a current of 5.0 mA. The sensitivity used for recording the spectra was 25  $\mu\text{V}$ .

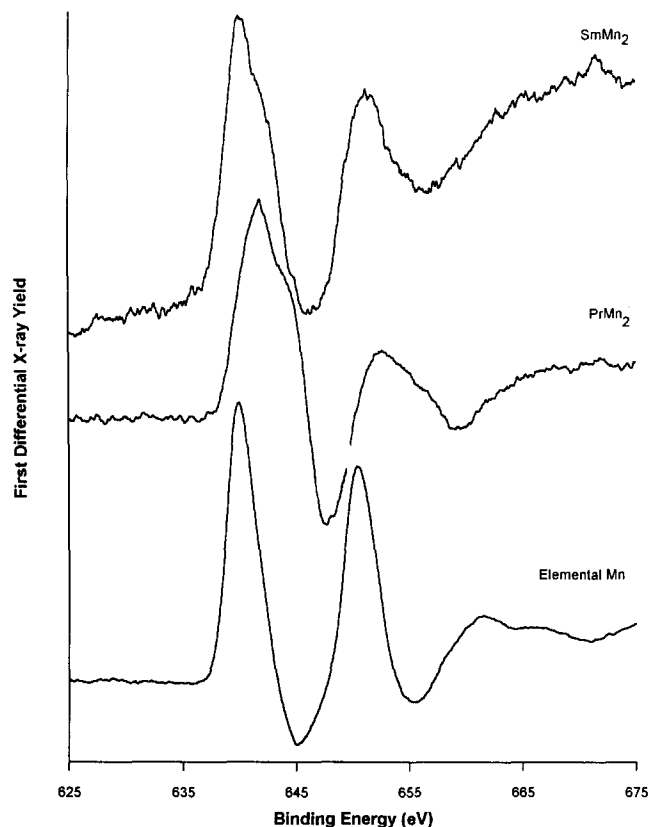


Fig. 2.  $L_{2,3}$  level SXAPS spectra of Mn in the elemental state and in the intermetallics  $\text{PrMn}_2$  and  $\text{SmMn}_2$ . The spectra were recorded with a current of 5.0 mA. The sensitivity used for elemental Mn and for  $\text{PrMn}_2$  was 10  $\mu\text{V}$  while for  $\text{SmMn}_2$  it was 2.5  $\mu\text{V}$ .

of SXAPS [23,24]. The model proposed to explain the presence of the intense peak in rare earth SXAPS spectra is the scattering resonance represented by  $3d^{10}4f^n + e \rightarrow 3d^9 4f^{n+2}$  transition. The  $3d_{3/2}$  peak ( $M_4$  peak) is observed to be broader than the  $3d_{5/2}$  peak ( $M_5$  peak). This is due to the Coster–Kronig transitions. The present measurements are therefore confined to the  $M_5$  level.

The corresponding SXAPS spectra in the  $L_{2,3}$  levels of Mn in elemental and the intermetallic  $\text{PrMn}_2$  are shown in Fig. 2. The spin–orbit splitting for elemental Mn is about 11 eV. Therefore the  $L_3$  structure is slightly superimposed on the high BE side with the  $L_2$  structure. The measurements are therefore confined to the  $L_3$  level. The intermetallic spectrum shows a distinct splitting of about 3 eV for each of the levels. This splitting is due to the crystal field and is under investigation by X-ray absorption spectroscopy. The corrected BEs of the  $M_5$  level of Pr in the elemental and the intermetallic are listed in Table 1. Table 2 lists the corresponding values for the  $L_3$  level of Mn. These core levels exhibit a positive chemical shift in this intermetallic.

The  $M_{4,5}$  core level spectra of Sm in elemental form and in the intermetallic  $\text{SmMn}_2$  are shown in Fig. 3.

Table 1

Data on  $M_5$  levels of rare earths in elemental and in  $\text{RMn}_2$  intermetallics; values of  $\Delta E_c$  are calculated from eq. (1); all values are in eV

Rare earth	Binding energy		$\Delta E$	$E_F$	$\Delta E_c$	
	Elemental	$\text{RMn}_2$			Elemental	$\text{RMn}_2$
Pr	926.0	926.4	+0.4	7.16	10.02	−2.46
Sm	1075.7	1074.8	−0.9	7.37	10.46	−3.99
Gd	1181.8	1182.2	+0.4	7.4	10.65	−2.85

Table 2

Data on  $L_3$  level of Mn in elemental and in  $\text{RMn}_2$  intermetallics;  $E_F$  for elemental Mn is 14.25 eV;  $\Delta E_{\text{ch}} = (E_F)_{\text{comp}} - (E_F)_{\text{elem}}$ ; all values are in eV

Sample	Binding energy	$\Delta E$	$\Delta E_{\text{ch}}$	$\Delta E_c$
Elemental	637.7	—	—	—
$\text{PrMn}_2$	638.2	+0.5	−4.2	+4.7
$\text{SmMn}_2$	637.4	−0.3	−3.8	+3.5
$\text{GdMn}_2$	638.2	+0.5	−3.6	+4.1

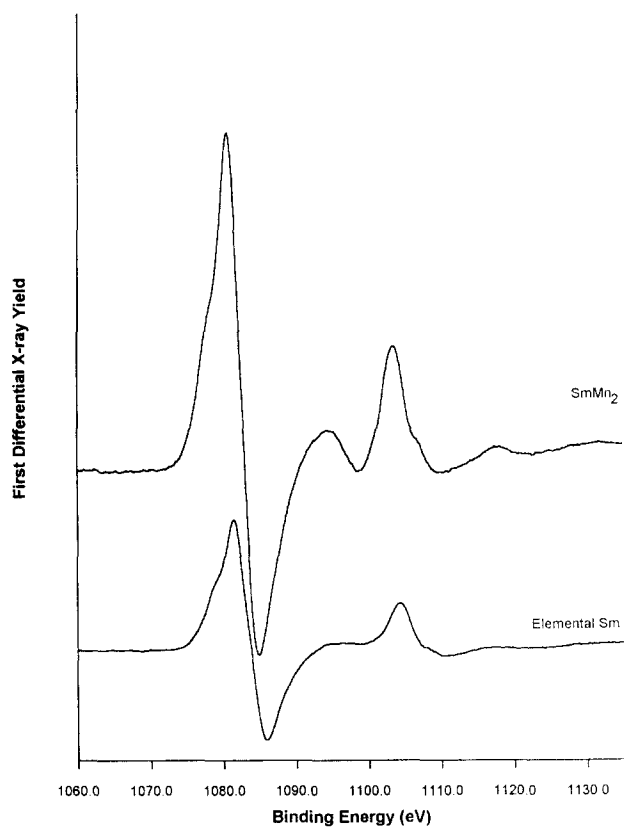


Fig. 3.  $M_{4,5}$  level SXAPS spectra of Sm in the elemental state and in the intermetallic  $\text{SmMn}_2$ . In this case the sensitivity for elemental spectra was  $100 \mu\text{V}$  and that for the intermetallic was  $25 \mu\text{V}$ .

The spin-orbit splitting in this case is 25.4 eV for elemental Sm and 26.3 eV for Sm in the intermetallic. The  $L_{2,3}$  spectra of Mn in this compound are included in Fig. 2. The BEs for Sm are listed in Table 1 and for Mn in Table 2. In this case both the  $M_5$  level of Sm and the  $L_3$  level of Mn show negative chemical shifts.

In a compound between a rare earth and a transition metal two effects are supposed to take place: (a) a charge transfer among the constituents and (b) a 3d–5d hybridization. The Pauling electronegativities for these elements are:  $\chi_{\text{Mn}} = 1.55$ ,  $\chi_{\text{Pr}} = 1.33$  and  $\chi_{\text{Sm}} = 1.17$ . Since Mn is more electronegative, there should be a charge transfer from the rare earths to Mn in these intermetallics. Based on this criterion it is expected that the rare earth core levels exhibit a positive chemical shift and the Mn core level a negative chemical shift if the charge transfer were solely responsible for the observed shift. The results on the experimentally observed shift are not consistent with these conclusions. This confirms that R–T charge transfer is not the dominating process upon alloying, leaving the 3d–5d hybridization as the main effect [25,26].

The BE of a core level electron is determined by the attractive potential of the nucleus and the repulsive Coulomb interaction with all the other electrons. The

core level shifts will therefore be due to the rearrangement of the valence electrons and the chemical environment changes of the central atom as a result of compound formation. Neglecting the screening effect, since all the samples considered here are good metals, the experimentally observed shift  $\Delta E$  can be expressed as

$$\Delta E = \Delta E_c + \Delta E_{\text{ch}} \quad (1)$$

where  $\Delta E_c$  is the contribution due to the configuration changes or the effect of hybridization and  $\Delta E_{\text{ch}}$  is the chemical shift due to charge transfer.

The charge transfer among the constituents produces changes in  $E_F$ . The Fermi energies in elemental Mn, Pr, Sm, and in the compounds  $\text{PrMn}_2$  and  $\text{SmMn}_2$  have been estimated using the free electron theory approximation. The values of  $E_F$  thus calculated are listed in Table 1. The  $\Delta E_{\text{ch}}$  values were determined by computing the difference  $(E_F)_{\text{compd}} - (E_F)_{\text{metal}}$ . This difference is observed to be positive for the rare earths and negative for Mn in these intermetallics. These Fermi level shifts as a result of charge transfer are in agreement with the Pauling electronegativity criterion.

The values of  $\Delta E_c$ , the shift due to hybridization or configuration changes, were obtained from Eq. (1). These values for rare earths are given in Table 1 and for Mn in Table 2. From these tables we observe that these values are positive for Mn but negative for the rare earths in the intermetallics. In SXAPS the core level electrons in transition metals are excited to the 3d bands which may hybridize with the 5d bands of the rare earths. However, in the case of rare earths the spectra represent the transitions to the sharp 4f core levels. Therefore, analysis of the 3d core levels of Mn are considered here to study the effect of hybridization between the 3d and 5d bands on the magnetic properties of these intermetallics.

In the R–T intermetallics the direct overlap between the 3d and 4f spins is small because the 4f shells are spatially localized. The R–T interactions occur through the intra-atomic 4f–5d and interatomic 5d–3d exchange interactions, as proposed by Campbell [10]. More recently Campbell's suggestions were confirmed by Brooks et al. [11–13] by performing self-consistent energy band calculations on various R–3d systems. According to this model the localized 4f spins create a positive localized 5d moment through the 4f–5d exchange and a negative localized moment through the direct 5d–3d exchange. These interactions therefore lead to ferromagnetic ordering if R is a light rare earth, or ferrimagnetic ordering if R is a heavy rare earth.

The 3d–5d hybridization significantly influences the 3d–5d band structure and relative magnitude and sign of the spin polarization at R and T sites. In the R–T intermetallics the pure 3d and 5d bands will hybridize to form hybridized regions at the top of the 3d band

and at the bottom of the 5d band. In the case of Mn the 3d band is split into a lower  $t_{2g}$  state and an upper  $e_g$  state [27]. This splitting lowers the energy of the spin-up 3d states reducing the 3d–5d hybridization for these states. However, the occupation number of the spin-down states will increase as a result of this hybridization. The induced 5d moment is therefore antiparallel to the 3d moment and related to the 5d occupation number,  $n_{5d}$  that is induced by the hybridization [11,12]. From the data in the Table 2 we observe a decreasing trend in the values of  $\Delta E_c$  in the case of light rare earths. This indicates that either the number of electrons decreases or more electrons are paired in the hybridized 3d–5d bands. We expect a decrease in the number of electrons. This can be interpreted to be a consequence of the lanthanide contraction influencing the 3d–5d hybridization. Owing to the contraction of the 4f shell with increasing R atomic number the shielding of the 5d states from the nucleus increases and raises their energy which leads to a reduction of the 3d–5d hybridization and to less charge transfer to the 5d states.

The number of electrons in the 5d band is 2.2, 2.1 and 1.9 respectively for Pr, Sm and Gd [28]. The reduction of  $n_{5d}$  with increasing R atomic number has also been reported for heavy RFe<sub>2</sub> compounds [12]. Similarly, a continuous reduction of the 3d moment was found with increasing atomic number. As long as a spontaneous moment is present on the Mn sites a similar behavior is to be expected for RMn<sub>2</sub>. Thus, for the light RMn<sub>2</sub> compounds the analysis of our SXAPS data in connection with the 5d–3d hybridization is in accordance with the experimental data reported in the literature [1–8]. It will be of considerable interest to study the behavior of those compounds in the vicinity of the so-called critical distance. This contains R = Tb, Dy, and Ho, where the character of the 3d moment changes from a spontaneous to an induced one. This particular problem will be a matter of future studies.

In summary, we have studied the electronic structure of PrMn<sub>2</sub> and SmMn<sub>2</sub> intermetallics using SXAPS. The core level shifts of the constituents have been utilized to estimate the shifts due to the hybridization of Mn 3d and R 5d bands. The decrease in this shift as a function of Z of the rare earth element is due to the decrease in the number of electrons in the hybridized bands. This leads to a decrease in the Mn magnetic moment in these intermetallics.

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