



Charge distribution and hyperfine interactions in the vicinity of impurity sites in In_2O_3 doped with Fe, Co, and Ni



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ABSTRACT

In this paper, first-principles calculations based on density functional theory (DFT) were used to determine TM (TM=Fe, Ni, Co) and Cd impurity locations in the In_2O_3 host structure, their charge states, the electronic and structural relaxations induced in the host lattice as well as to interpret previous and supplementary experimental results of hyperfine interactions. Different techniques were carried out to characterize TM-doped In_2O_3 bulk samples prepared by the sol–gel method starting from very pure metals. Perturbed angular correlation (PAC) spectroscopy, a sensitive nuclear technique capable of measuring interactions from electronic charge and spins within an atomic distance, was used to experimentally determine hyperfine interactions at cation sites of In_2O_3 doped with Co and Ni using $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ as probe nuclei. Room temperature results of magnetization measurements in In_2O_3 doped with Fe, Co and Ni show ferromagnetic ordering coexisting with a paramagnetic behavior for all samples. Results of PAC spectroscopy and DFT calculations show that TM atoms locate as second nearest neighbors of Cd probes preferentially occupy symmetric sites of the doped In_2O_3 crystal structure with lattice parameters slightly different from that of pure In_2O_3 . Moreover, while a major population of ^{111}Cd probes observes almost the same hyperfine interactions measured for pure In_2O_3 , a small population detects magnetic dipole interactions with magnetic hyperfine field at Cd probes of 2.6 T, 3.1 T, and 4.6 T, respectively for Ni, Co, and Fe doping presenting an almost linear dependence on the number of unpaired 3d electrons of the transition metal impurity.

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1. Introduction

Wide band-gap semiconductor oxides such as In_2O_3 are good candidates for important technological applications such as gas sensing [1], thin-film transistors [2], and optoelectronic devices [3]. The doping with other elements than the native cation can enhance certain properties of these oxides and turn those better materials for specific applications or make them suitable for new ones. However, it was the possibility of occurrence of room temperature ferromagnetism in semiconductor oxides doped with transition metals that make them emerged as a possible candidate for dilute magnetic semiconductors.

The search for a magnetic semiconductor started in the

beginning of the 1960s [4] and intensified only 30 years later with the observation of ferromagnetism in III–V semiconductors doped with transition metals [5,6]. As the highest Curie temperature observed in these compounds was 172 K [6], reports of room temperature ferromagnetism, theoretically predicted for ZnO doped with 5% of Mn [7] and experimentally observed in TiO_2 doped with 2% of Co [8], have boosted the interest in dilute magnetic semiconductor oxides, which continues to date due to their magnetic, electric and optical properties. However, the occurrence of room temperature ferromagnetism in TM-doped semiconductor oxides has been controversial with contradictory results [9–13]. Ferromagnetism in TM-doped semiconductor oxides has been ascribed to metallic TM clusters in the oxide matrix [14,15], secondary phases [16], or to uncontrolled spurious sources [17]. Reports on convincing experimental works using atomic resolution techniques have contributed to form an almost generally accepted picture where TM atoms are at substitutional sites of the semiconductor oxide presenting a paramagnetic behavior and the observed ferromagnetism is supposed to be due to the polarization of donor electrons trapped in oxygen vacancies [10,13,18–21].

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A significant difference in the magnetic behavior has also been observed between thin film and bulk samples [16,22,23], with the magnetization for the ferromagnetic component being much smaller in bulk than in thin films [24]. This observation is compatible with the assumption that the existence of oxygen vacancies is responsible for the ferromagnetism since there is much more probability of occurrence of vacancies in thin films than in bulk samples due to the larger surface area to volume ratio in thin film than in bulk samples. Following this assumption, Straumal et al. [25] showed that the magnetization in Mn-doped ZnO correlates with the area of grain boundaries in nanostructured samples. Nevertheless, there is not, so far, a definitive theoretical description of the mechanism that causes the ferromagnetism in the TM-doped semiconductor oxides. In an attempt to explain the coupling mechanism in ferromagnetic TM-doped semiconductor oxides with TM concentration far below the percolation limit, Coey et al. [26] proposed a model in which the exchange coupling is mediated by donor electrons in structural defects such as oxygen vacancies [27]. These electrons form bound magnetic polarons within an expanded orbit that overlap forming a spin-split impurity band populated by charge transfer from a proximate charge reservoir. However, the lack of quantitative experimental data on the local magnetism and the electronic structure within the ferromagnetic region has prevented the formulation of a theoretical description of this phenomenon. New experimental data of these categories are, therefore, necessary and techniques sensitive enough to identify them from different regions within samples on an atomic scale are welcome. Basic questions need answer: Why the magnetic behavior is different for thin films and bulk samples. Are there regions inside homogeneous samples that are ferromagnetic and regions that are not?

Among the semiconductor oxides, In_2O_3 has been less investigated when compared with other semiconductor oxides such as ZnO, SnO_2 and TiO_2 , mainly because it has the most complex structure with two nonequivalent cation sites. In_2O_3 is an excellent material with a high potential to integrate electronic and photonic properties in a single device because its well-known properties: it is a n-type wide band gap transparent semiconductor with a high electron carrier density. The introduction of few percent of a magnetic 3d-element in the In_2O_3 matrix can add to this material the capability to integrate magnetic properties to future devices [28,20,29].

When semiconductor oxides are doped with other elements, the resulting effect on the host structure must be investigated. Therefore, the first purpose of the work reported in this paper was to investigate the doping mechanism of the semiconductor In_2O_3 with different 3d-transition metals to determine the impurity site location in the host structure, its charge state, and electronic and structural relaxations induced in host lattice. Specifically, it is important to verify if these metals form other phases within the In_2O_3 matrix or if they replace In positions in the crystallographic sites. Since they are in substitutional sites, it is important to determine if the impurities are homogeneously distributed following the 3:1 crystallographic ratio of the cation occupation in the bixbyite structure or if there is a preference for one of the two nonequivalent In positions in the In_2O_3 unit cell. In addition, it is fundamental to investigate the effect of doping on the local structure of the dopant's neighborhood as well as the electronic structure at the impurity sites. The second purpose was to observe the existence of magnetism in the TM-doped In_2O_3 and, if the magnetism exists, try to determine its origin.

The experimental determination of the 3d-dopant site preference in In_2O_3 may be directly achieved by local techniques that can obtain data within an atomic range. However, some techniques such as XAFS are not able to unambiguously determine site preferences when the dopant is much smaller than the host In

atom [30]. Perturbed angular correlation (PAC) spectroscopy is a hyperfine interactions technique, which is particularly useful to investigate In_2O_3 because it can use $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ as probe nuclei at In sites and, therefore, it is capable of providing data from site fractions at different regions inside the whole sample. In a previous paper, PAC spectroscopy was used to measure hyperfine interactions in In_2O_3 doped with Fe [31] and the results show the existence of three site fractions, two of them corresponding to probe nuclei at the two nonequivalent sites of In_2O_3 and a third fraction that was associated to probe nuclei with Fe atoms in their neighborhood.

In the current paper, we investigated In_2O_3 doped with Co and Ni by PAC spectroscopy to compare the results with those for Fe doping as well as we performed theoretical calculations using the WIEN2k code [32], which is an implementation of the FP-APW+lo method within the Density Functional Theory (DFT), to simulate In_2O_3 doped with Fe, Co and Ni. Additional magnetic measurements were carried out in doped samples to characterize their magnetic properties. In this paper it will be shown that the theoretical interpretation of experimental data indicates that TM impurities prefer one of the two nonequivalent sites of In_2O_3 and magnetic interactions were experimentally observed by probe nuclei at next nearest neighbor sites to TM impurities and in the vicinity of oxygen vacancies.

2. APW+lo calculations

The In_2O_3 unit cell of the Bixbyite structure has 80 atoms, 48 oxygen atoms and 32 indium atoms (Fig. 1a). In this structure In atoms are distributed in two different crystallographically unique cation sites: sites 24d with 24 In atoms and sites 8b with 8 In atoms (hereafter referred as sites *Ind* and sites *Inb*, respectively). Sites *Inb* present axial symmetry (point group -3) and are coordinated with six equivalent nearest neighbors (NN) oxygen atoms ($\text{O}_{1\text{NN}}$). Sites *Ind* are highly asymmetric (point group 2) and are surrounded by six oxygen atoms arranged in three pairs of $\text{O}_{\text{NN}i}$ ($i=1, 2, 3$) neighbors where the In– $\text{O}_{\text{NN}i}$ distances (d_i) satisfy the relation $d_1 < d_2 < d_3$. The In– O_{NN} coordination is shown in Fig. 1b. The symmetric sites *Inb* also have 12 $\text{In}_{2\text{NN}}$ second nearest neighbors, all located at sites *Ind*, these $\text{In}_{2\text{NN}}$ are grouped in two sets of six In equivalent atoms each ($\text{In}_{2\text{NN}1}$ and $\text{In}_{2\text{NN}2}$). On the other hand, the asymmetric sites *Ind* present 12 $\text{In}_{2\text{NN}}$ second nearest neighbors, four of which are at sites *Inb* and the other eight In atoms are at sites *Ind* as one can observe in Fig. 1c.

In order to investigate the effect produced by the TM doping in the Cd-doped In_2O_3 host matrix, we have performed theoretical calculations using the full-potential augmented plane wave plus local orbital (FP-APW+lo) method [33] based on the density functional theory [34] and implemented in the WIEN2k code [32]. The exchange and correlation effects were taken into account by Generalized Gradient Approximations as implemented in WC-GGA [35] in the majority of our calculations or by PBE-GGA [36]. Both these implementations give similar results for the purposes of the present work, as reported in the literature [37,38]. The muffin-tin radii adopted in the calculations were 0.99 Å for TM atoms, 1.02 Å for Cd and In atoms and 0.90 Å for O atoms. The $R_{\text{mt}} K_{\text{max}}$ parameter, which controls the size of the basis set, was chosen to be $R_{\text{mt}} K_{\text{max}} = 7$ in all the calculations. The integration in the reciprocal space was carried out using the tetrahedron method and taking 27k-points ($3 \times 3 \times 3$) in the first Brillouin zone. When the self-consistency was achieved, the forces on the ions were determined, the ions displaced, and the new atomic positions obtained. This process was repeated until the forces on the ions were below a tolerance value of 1 mRy/au. In each step of the self-consistent calculation, the principal component (V_{zz}) of the electric field

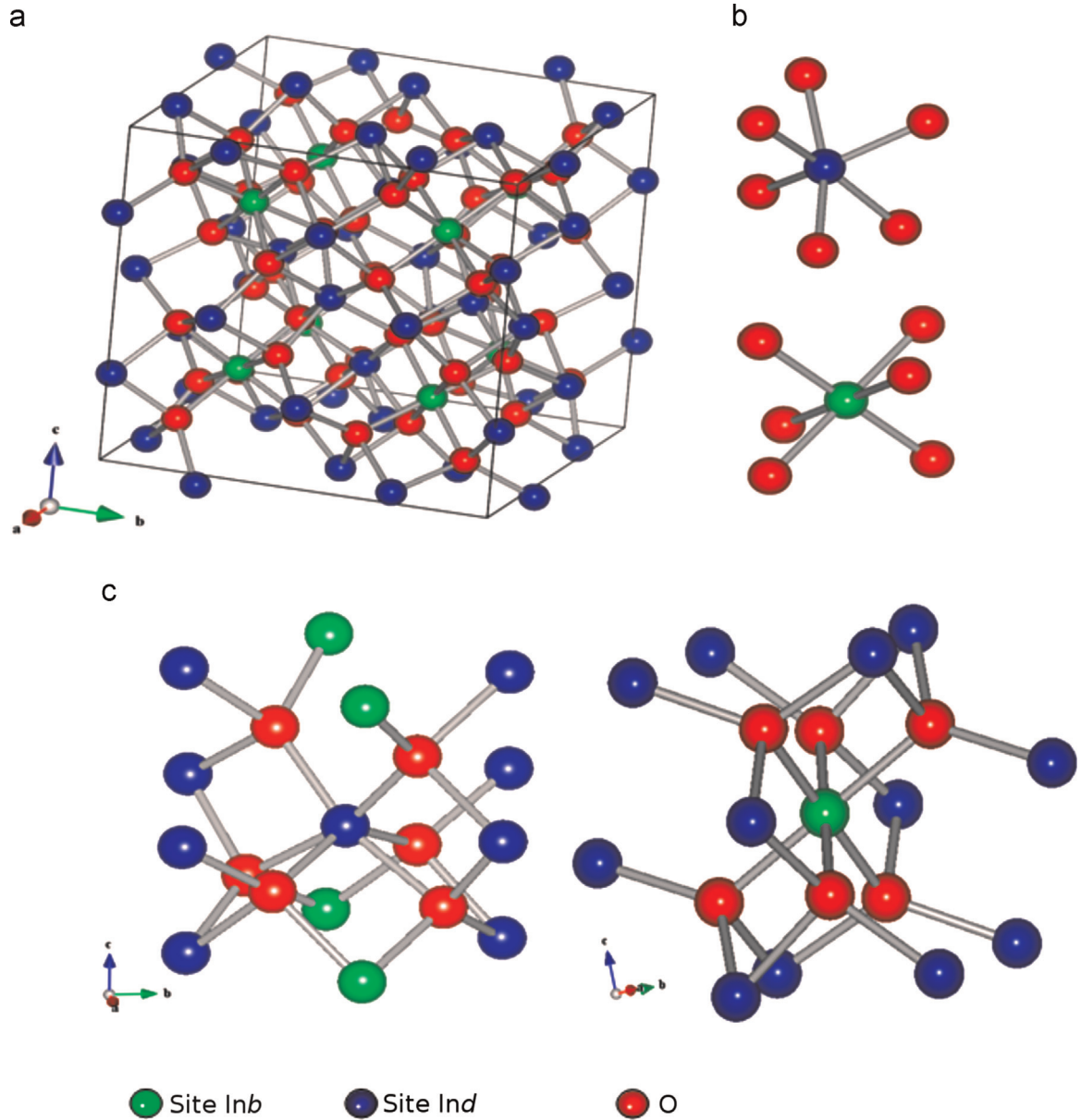


Fig. 1. (a) Bixbyite unit cell, the red spheres represent the O atoms, the green spheres represent the Inb -type cation sites and the blue spheres are the Ind -type cation sites. (b) O_{NN} coordination of the Ind -type cation site (top) and of the Inb -type cation site (bottom). (c) In_{NN} coordination of the Ind cation site (bottom left) and of the Inb cation site (bottom right). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

gradient (efg) tensor was determined from the expansion of the potential into harmonic coefficients [32].

This methodology was used in three different doped systems: (1) TM-doped In_2O_3 (TM=Fe, Co, Ni) cell; (2) Cd-doped In_2O_3 cell; (3) In_2O_3 cell doped with both Cd and Fe. In the first system we performed APW+lo calculations with two different TM dilutions in the TM-doped In_2O_3 cell (see Section 4.1). In one configuration we have replaced (separately for the site Ind and for the site Inb) one In atom of the unit cell by one TM impurity simulating a dilution of 1:32 that represents a TM concentration of 3%. And, in another configuration, we replaced one In atom in half of the unit cell by the one TM impurity simulating now a dilution of 1:16 (TM concentration of 6%). For this later dilution, we performed an additional calculation where spin polarization was taken into account in the DFT calculations (SDFT) where TM also replaces separately In atom at site Ind or at site Inb . The second system was used to calculate the efg tensor at Cd impurities located in cation sites of the In_2O_3 bixbyite structure (see Section 4.3). In this

simulation we have considered a In_2O_3 unit cell where only one In atom (belonging to site Ind or Inb in two different calculations) was replaced by one Cd atom (1:32 dilution). (3) Finally, to reproduce the hyperfine parameters observed by the $^{111}In(^{111}Cd)$ probes in the TM-doped In_2O_3 semiconductor and measured by PAC spectroscopy, we carried out APW+lo calculations in a Cd and Fe co-doped In_2O_3 unit cell where the Cd was located at the cation site and the TM impurity was located as second nearest neighbor of the Cd impurity replacing an In_{2NN} atom (see Section 4.3).

3. Experimental procedure

Synthesis details: TM-doped (TM=Ni, Co) In_2O_3 samples were prepared using the well-known Pechini sol-gel method. In, Co, and Ni (99.9999% of purity) metals were separately dissolved in dilute solutions of nitric acid. In_2O_3 samples doped with 5% of Co and Ni were prepared by adding citric acid to a mixture of

appropriate quantities of indium nitrate and metal dopant solutions. Each mixture was stirred and heated at 353 K until the gel formation, which was slowly heated to 673 K and calcined for 10 h in air. The resulting powder was calcined at 973 K for 12 h, subsequently pressed into a small pellet and heated again at 973 K for 10 h. The concentration of the dopant in each sample was determined by X-ray fluorescence (Panalytical Axios advanced spectrometer) and the results showed a concentration of 4.8%, 4.9%, and 5.4% for Fe, Co, and Ni, respectively.

Characterization: After preparation, all samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and magnetization measurements. In order to perform perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC) measurements, a drop of radioactive $^{111}\text{InCl}_3$ solution was deposited on the surface of a fraction of the pellet of each sample which was sealed in an evacuated quartz tube (4×10^{-4} mbar) and heated at 723 K for 12 h to diffuse

the radioactive ^{111}In . Finally, the samples were further heated at 973 K for 12 h in air. PAC-spectroscopy measurements were carried out with a conventional fast-slow coincidence set-up using four BaF_2 detectors as a function of temperature from 295 K to 1073 K and at 77 K using the well-known 133–245 keV gamma-gamma cascade of ^{111}Cd , the daughter nucleus from the electron capture of ^{111}In .

XRD measurement of pure and TM-doped In_2O_3 (TM=Fe, Ni, Co) powder was carried out after calcination at 973 K using $\text{CuK}\alpha$ radiation ($\lambda_{\alpha_1}=0.154060$ nm and $\lambda_{\alpha_2}=0.154443$ nm), and the resulting spectra were analyzed by the Rietveld method. SEM and EDS measurements were carried out on the pellets of the same samples using a scanning electron microscope Quanta 600FEG – FEI. The magnetic measurements were made using the vibrating sample magnetometer (VSM) option of a Physical Property Measurement System (PPMS) from Quantum Design. The temperature range of sample measurements was from 5 K to 300 K and

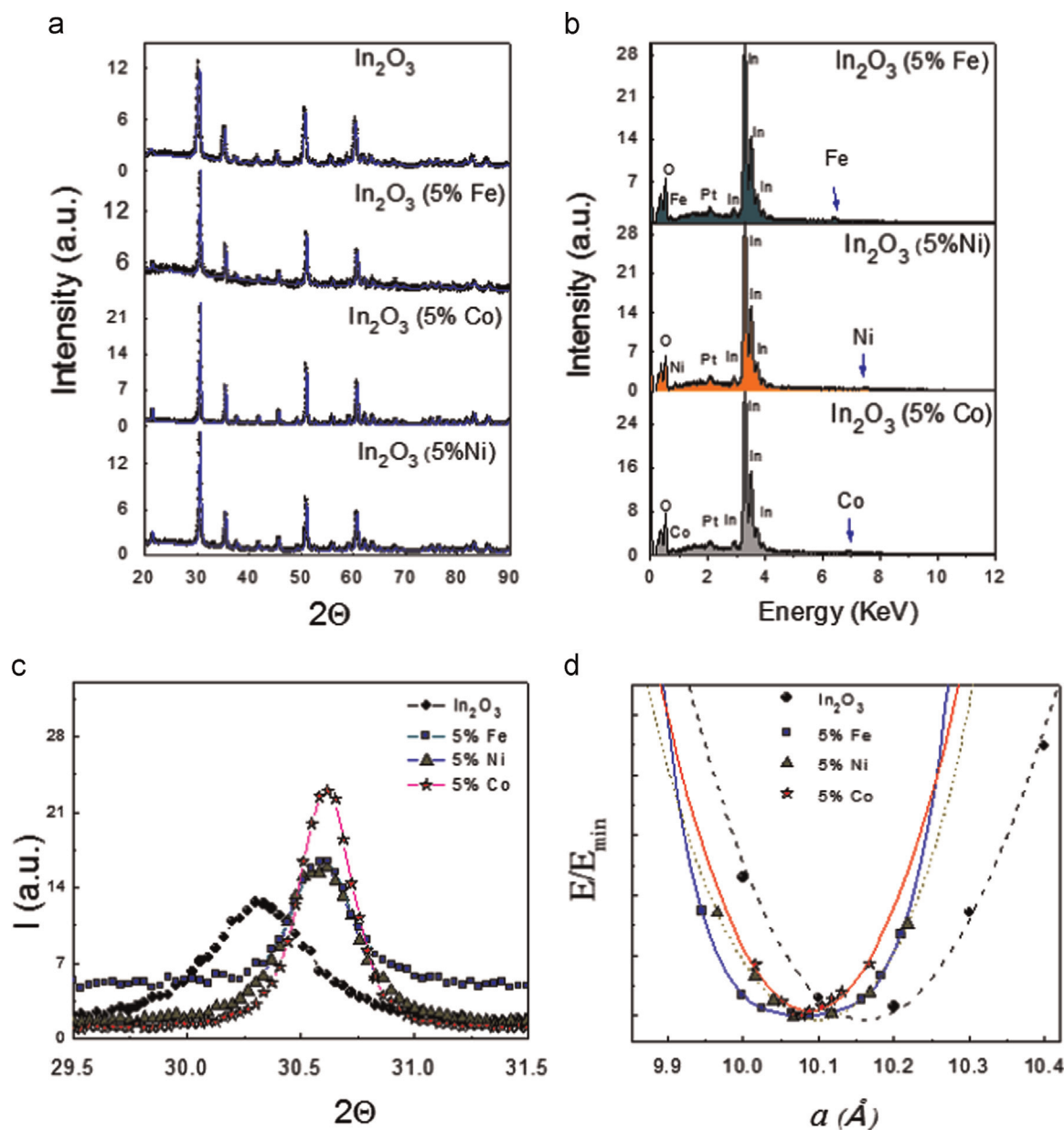


Fig. 2. (a) XRD in powder sample at room temperature for pure In_2O_3 and TM-doped In_2O_3 (TM=Fe,Co,Ni). The solid lines represent the calculated XRD pattern using the Rietveld method. (b) EDS in TM-doped In_2O_3 powder samples. (c) Line (222) of the XRD pattern for pure and TM-doped In_2O_3 (TM=Fe, Ni, Co). (d) $E/E_{\min}$ vs. a for TM located at site Inb in doped In_2O_3 . Data for pure and Fe-doped In_2O_3 were taken from Sena et al. [31].

applying magnetic fields up to 90 kOe.

4. Results and discussion

4.1. Bixbyite structure

4.1.1. X-ray diffraction results

The resulting XRD patterns for studied samples are shown in Fig. 2a where data for pure and Fe-doped In_2O_3 were taken from Sena et al. [31]. The solid lines in the diffraction patterns represent the fit obtained by the Rietveld method. To search for secondary phases we look for small peaks in the 2θ region of XRD spectra where highest intensity lines of pure TM or expected TM compounds would be. As no traces of such lines were found, it is possible to assure that, within the resolution of XRD measurements, no secondary phases were observed and the Rietveld analysis revealed the formation of a single phase in the cubic bixbyite structure, corresponding to the space group $la\bar{3}$ for all samples. Lattice parameters obtained from the fit for each TM-doped In_2O_3 sample at room temperature are $a_{\text{Fe}}=10.108$ Å, $a_{\text{Co}}=10.110$ Å, and $a_{\text{Ni}}=10.117$ Å, for Fe, Co, and Ni doping, respectively, which are somewhat smaller than that for pure In_2O_3 sample, which was found to be $a=10.151$ Å ($a_{\text{Fe}} < a_{\text{Co}} < a_{\text{Ni}} < a_{\text{pure}}$). This is a consequence of the ionic radius (R) of TM in a six-coordinate octahedral sublattice when compared with that for In ($R_{\text{Fe}} < R_{\text{Co}} < R_{\text{Ni}} < R_{\text{In}}$) [39]. Interestingly, this size relation between ionic radii is the same as that for lattice parameters only when the valence for TM ions is +2 except for Fe, which valence +3 also follows this systematic. Since XRD patterns did not show any other oxide phases, it was assumed that Fe, Co, and Ni elements replaced homogeneously In positions in the crystal lattice. The decrease in the lattice parameters of doped samples is a strong indication that TM ions are incorporated into the cation sites of In_2O_3 [28]. EDS spectra (Fig. 2b) and SEM images taken from different regions of the same sample showed that all samples are homogeneous without significant impurities and absence of secondary TM oxide phases.

4.1.2. APW+lo results: optimization of lattice parameter

To evaluate the observed decrease in the lattice parameter a of the bixbyite structure due to the doping with TM impurities in In_2O_3 oxide, we have performed an optimization within the WC-GGA approximation with two different TM-doped In_2O_3 dilutions, 1:32 (corresponding to 3% doping) and 1:16 (corresponding to 6% doping). First, such calculations were performed in In_2O_3 doped with Ni. Results for Ni impurities at the site *Ind* showed lattice parameters of $a=10.1307$ Å for 3% doping and $a=10.1059$ Å for 6% doping. A comparison of these results with those predicted by APW+lo WC-GGA calculations for pure In_2O_3 , for which the lattice parameter is $a=10.162$ Å, shows that Ni doping with a dilution of 1:32 (3%) produces a reduction in the lattice parameter of 0.30%, while the 1:16 (6%) dilution produces a reduction of 0.55%. It was, therefore, observed that the increase in the Ni concentration produces a decrease in the lattice parameter of the doped oxide when compared with pure In_2O_3 . To extend this investigation to other TM-doped In_2O_3 oxides, we carried out a set of the APW+lo calculations in In_2O_3 doped with Fe and Co (with a dilution 1:16). The resultant total energy (E/E_{min}) of the doped cell was plotted as a function of the lattice parameter for each dopant (see Fig. 2d) and compared with that for pure In_2O_3 (see Fig. 2c). The most intense line in the XRD spectrum at $2\theta \sim 30^\circ$, corresponding to the (222) spectral line, for pure and TM-doped In_2O_3 samples, is also shown in Fig. 2c. The plot clearly shows a shift in the position of the (222) peaks to higher angles for all doped samples when compared to pure In_2O_3 . This effect is certainly due to a decrease

Table 1

Lattice parameter (a_{min}), self-consistent-field energy of the relaxed structure (E_{min}), percentage reduction of the lattice parameter ($\Delta a/a$), and the average atomic distance ($d_{\text{TM-O}}$) between the TM and the oxygen nearest neighbor calculated with the APW+lo method in the WC-GGA approximation for the cases of TM-doped In_2O_3 (TM=Ni, Co, Fe) with a dilution of 1:16 (6%). The absolute values of the energies do not have physical significance, only their differences do.

TM	Site	a_{min} (Å)	E_{min} (Ry)	$\Delta a/a$ (%)	$d_{\text{TM-O}}$ (Å)
Fe	<i>Ind</i>	10.0841	−182,628.522	0.76	1.95834
Fe	<i>Inb</i>	10.0858	−182,628.546	0.75	2.05462
Co	<i>Ind</i>	10.0921	−182,869.836	0.68	2.11138
Co	<i>Inb</i>	10.0802	−182,869.902	0.80	2.09815
Ni	<i>Ind</i>	10.1059	−183,124.564	0.55	2.08863
Ni	<i>Inb</i>	10.1006	−183,124.579	0.60	2.19151

in the inter-planar spacing of the corresponding planes indicating a diminution of lattice parameter $a_{\text{Fe}} < a_{\text{Co}} < a_{\text{Ni}} < a_{\text{pure}}$. This behavior is similar to that observed in the plot of the E/E_{min} vs. a predicted from the APW+lo WC-GGA results.

Table 1 displays the self-consistent-field energies of the relaxed TM-doped In_2O_3 structures (E_{min}), the lattice parameters corresponding to these energies (a_{min}), and the relaxation produced in the host structures obtained from the DFT calculations for each TM-doped In_2O_3 semiconductor. The results correspond to 1:16 dilution calculations and were performed with the WC-GGA approximation. From DFT calculations, it was observed that the E_{min} reaches a minimum value for the simulation where the TM impurity is located in the site *Inb*. Similar results were obtained with SDFT calculations where one Fe atom replaces In atom at site *Ind* or site *Inb*, Fe at site *Inb* is ~ 50 mRy smaller than the supercell in which Fe replaces In at site *Ind*. From the relaxation of the unit cell, it was noticed that the TM doping produces a reduction of the lattice parameter. Supposing that TM impurities are randomly located in the In_2O_3 host lattice, the TM doping will satisfy the *Ind*:*Inb* (3:1) crystallographic ratio of the bixbyite structure. In this case the lattice parameters predicted by the APW+lo calculations are $a_{\text{Ni}}=10.1046$ Å, $a_{\text{Co}}=10.0891$ Å and $a_{\text{Fe}}=10.0845$ Å, which are, therefore, in agreement with the ordering of lattice parameters measured with X-ray diffraction: $a_{\text{Fe}} < a_{\text{Co}} < a_{\text{Ni}} < a_{\text{pure}}$. The table also displays the average bond length between the TM impurity and the nearest neighboring oxygen ions. The results show that these distances for all impurities are smaller than that for pure In_2O_3 , which are 2.21273 Å for *Inb* and 2.21907 Å for *Ind* and follow the same relation for the ionic radius (R) of TM in a six-coordinate octahedral sublattice ($R_{\text{Fe}} < R_{\text{Co}} < R_{\text{Ni}} < R_{\text{In}}$) when the TM are at the In b sites.

To interpret the structural and electronic relaxations induced by the magnetic TM impurities in the In_2O_3 semiconductor as well as to determine the localized magnetic moment at them, APW+lo calculations with the WC-GGA approximation taking into account the magnetic moment at TM muffin-tin (SDFT) were performed in TM-doped In_2O_3 (TM=Fe,Co and Ni) unit cell with a dilution of 1:16 (6%). Fig. 3 shows results for the total density of states (DOS) of the Fe-doped In_2O_3 supercell as well as the partial density of states (PDOS) with d symmetry of the Fe impurity. One can see that Fe-impurity bands are located on the top of valence band (VB) and on the bottom of conduction band (CB) and, consequently define the Fermi energy and the band gap. The band gap of In_2O_3 was determined to be 3.6 eV [40], while the band gap for Fe and Mn doped samples was experimentally shown to be narrower [41] than that for pure In_2O_3 . The largest contribution to the valence band comes from O atoms which points to the ionic character of the bixbyite In_2O_3 semiconductor. Essentially Fe and $\text{O}_{1\text{NN}}$ contributions are present in the impurity levels showing that the electronic states of the impurity level are spatially located at the

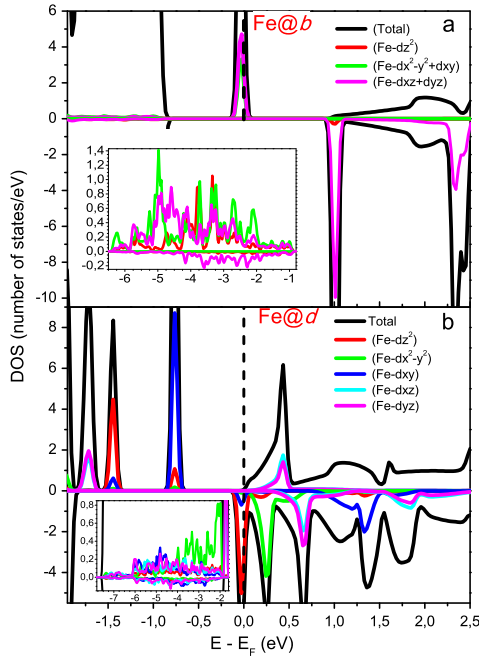


Fig. 3. DOS of the Fe-doped In_2O_3 for (a) Fe at site Inb and (b) Fe at site Ind . The insets display the corresponding PDOS of d sublevels of the Fe impurity.

Fe-O_{NN} surrounding. The DOS and PDOS plots for Fe atoms separately at sites Inb and sites Ind of the bixbyite structure of In_2O_3 are shown in parts (a) and (b) of Fig. 3. Due to the axial symmetry of sites Inb , the d sublevels of Fe are grouped in three energy bands: d_z^2 , $d_{x^2-y^2} + d_{xy}$, and $d_{xz} + d_{yz}$. With regard to Fe at sites Ind , five non-degenerate d sublevels are expected due to the lower symmetry when compared to sites Inb . For both sites, d sublevels show homogeneous hybridized portion for the majority spin (see insets in Fig. 3). PDOS plots also show that the $d_{x^2-y^2} + d_{xy}$ and $d_{xz} + d_{yz}$ sublevels define the Fermi energy and band gap for Fe at sites Inb , while d_{xy} and d_z^2 sublevels determine the Fermi energy for Fe at sites Ind with d_{xy} , d_{yz} , $d_{x^2-y^2}$ sublevels at the minimum of CB.

A visual inspection of Fig. 3 shows that there is no gap between these sub-levels and the bottom of the CB for Fe impurity at site Ind . This observation can be an artifact due to the known weaknesses of the DFT calculation to reproduce the gap values in semiconductors. However, even if a small real gap exists, one can expect that the electrons that occupies these sub-levels could be thermally excited into the CB and could interact via “spin-polarized conduction electron” with other Fe atom at sites Ind situated some distance apart. If the interaction is able to align the magnetic moments of both the Fe atoms, it could be concluded that Fe atoms at sites Ind in In_2O_3 are more likely to present magnetic order than Fe atoms at sites Inb via conduction electrons polarization.

4.2. PAC results using ^{111}Cd probe nuclei

The PAC spectra at room temperature in pure and TM-doped In_2O_3 (TM=Fe, Co and Ni) are shown in Fig. 4. The solid lines represent the fit of the model for the static electric quadrupole interaction given by

$$R(t) = A_{22}G_{22}(t) = A_{22} \sum_i f_i G_{22}^i(t), \quad (1)$$

where A_{22} is the angular correlation coefficient, f_i are the fractional site populations and $G_{22}^i(t)$ are the corresponding perturbation factors, which for static quadrupole interaction is given by

$$G_{22}(t) = S_{20} + \sum_{n=1}^3 S_{2n} \cos(\omega_n t) \exp(-\omega_n^2 \tau_R^2/2) \times \exp(-\omega_n^2 \delta^2 t^2/2), \quad (2)$$

where the transition frequencies ω_n and their amplitudes S_{2n} are a consequence of the hyperfine splitting of the intermediate nuclear level in the ^{111}Cd gamma-gamma cascade. All transition frequencies are related to the lowest transition frequency which depends on the nuclear quadrupole frequency $\omega_Q = eQV_{zz}/[4I(2I-1)\hbar]$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx} , V_{yy} and V_{zz} are the components of the efg tensor in its principal axis system, with V_{zz} being the largest component. Generally, the spin independent quadrupole frequency $\nu_Q = eQV_{zz}/h$, where Q is the nuclear electric quadrupole moment of the intermediate level, is used to calculate V_{zz} . For pure dipole magnetic interactions, the Larmor frequency ω_L is determined from $G_{22}(t)$, and the magnetic hyperfine field B_{hf} can be calculated from the relation $\omega_L = g\mu_N B_{\text{hf}}/\hbar$, where μ_N is the nuclear magneton and g is the g -factor of the intermediate level of ^{111}Cd . The effects of finite time resolution τ_R of detectors and the distribution of efg with a width δ are also properly taken into account. Detailed description of the experimental methodology used in PAC spectroscopy measurements can be found elsewhere [42,43]. The hyperfine parameters obtained from the fits to the experimental spectra are displayed in Table 2.

The room-temperature spectrum for pure In_2O_3 sample (see Fig. 4a) was fitted with a model given by Eqs. (1) and (2) considering two site fractions corresponding to the two non-equivalent cation sites of the In_2O_3 bixbyite structure. One site fraction with $\nu_{Qd} = 117(1)$ MHz, $\eta_d = 0.72(1)$ and $f_d = 75(5)\%$ was assigned to ^{111}Cd probe nuclei occupying In positions at sites Ind . The other site fraction with $\nu_{Qb} = 152(1)$ MHz, $\eta_b = 0$ and $f_b = 25(2)\%$ was assigned to probe nuclei at sites Inb . This results are in very good agreement with those early reported in the literature [44,45]. PAC spectra at room temperature for TM-doped In_2O_3 samples are somewhat different from that for pure sample, as can be visually seen in Fig. 4, and were fitted, in a first attempt, with a model where three site fractions were necessary. Results assigned to sites Ind and sites Inb yielded essentially the same values of hyperfine parameters (ν_Q , η , and frequency distribution δ) of those obtained for site Ind and site Inb of pure In_2O_3 sample, respectively. As an additional site fraction was needed to fit the model to the experimental data, the fractional site populations changed. This additional site fraction (hereafter identified as site 3) was characterized with a quadrupole frequency similar to that of site Inb at room temperature ($\nu_{Q3} \sim 152$ MHz) but with a non-zero asymmetry parameter ($\eta_3 \sim 0.45$) for all TM-doped samples with fractional site populations ranging from 34% to 47%, as displayed in Table 2. This interaction, therefore, could be assigned to ^{111}Cd probes at sites Inb but with a different neighborhood from that for a regular site Inb , probably due to the presence of a TM atom in their vicinity, however, the fractional site population analysis will be better discussed in Section 4.4.

Fig. 4e and f shows the PAC spectra for In_2O_3 doped with Co and Ni at some temperatures. The solid lines represent the fit of the theoretical model using pure quadrupole interactions. The temperature dependence of the hyperfine parameters for Co and Ni doped samples obtained from the fits is shown in Fig. 5 where are compared with data for Fe-doped In_2O_3 taken from Sena et al. [31]. Results for the temperature dependence of the hyperfine parameters for In_2O_3 samples doped with Fe and Ni show that values of ν_Q and η for site Ind and site Inb change very little with temperature. The quadrupole frequency of site 3 practically did not vary with temperature for both Fe- and Ni-doped samples and the asymmetry parameter for Ni-doped sample. For Fe-doped sample,

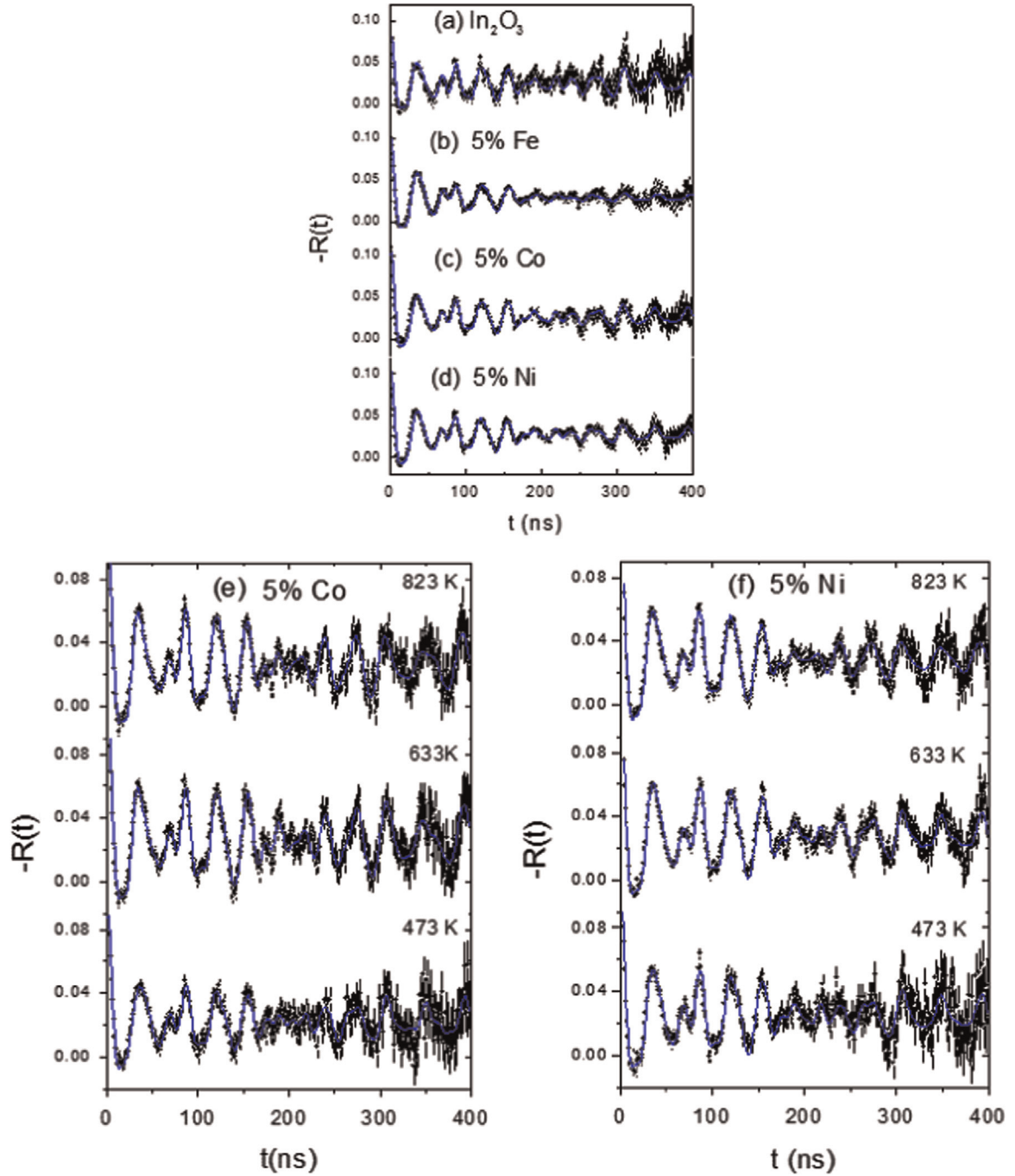


Fig. 4. PAC spectra for pure In_2O_3 and samples doped with 5% of Fe, Co and Ni at room temperature (a), (b), (c), and (d), respectively. PAC spectra at indicated temperatures for $^{111}\text{In}(^{111}\text{Cd})$ in In_2O_3 doped with 5% Co (e) and 5% Ni (f). The solid lines represent the theoretical fit using only quadrupole interactions. Data for pure (0%) and 5% Fe doped In_2O_3 samples are from Sena et al. [31].

η decreases little with the increase of temperature, as shown in Fig. 4. While the fraction population f_b varies very little for Ni- and Fe-doped samples, f_d gradually increases with the increase of temperature at expense of f_3 and, for Fe-doped sample, it recovers the value of $\sim 75\%$ of pure sample In_2O_3 at 1073 K.

The temperature dependence of hyperfine parameters for In_2O_3 doped with Co is similar to those for Fe- and Ni-doped samples concerning the values of ν_Q and η for site Ind and site Inb . However, the quadrupole frequency ν_{Q3} of site 3 decreases significantly from ~ 155 MHz to ~ 130 MHz when temperature increases from ~ 550 K to ~ 650 K. The asymmetry parameter of site 3 in the same temperature range, on the other hand, increases from $\eta_3 \sim 0.40$ to ~ 0.65 . This change in ν_{Q3} and η_3 values indicates a possible

unexpected structural transition in the environment around site 3 in that temperature range. As f_3 decreases while f_d increases with temperature, we suppose that part of probe nuclei at site 3 positions had their environment relaxed to that of site Ind .

4.3. Hyperfine interactions interpretation

To understand the hyperfine parameters obtained by PAC-spectroscopy measurements with ^{111}Cd in pure In_2O_3 , we have calculated V_{zz} , the largest component of efg tensor, at Cd sites for In_2O_3 unit cell doped with Cd ($\text{In}_2\text{O}_3:\text{Cd}$) for both, the neutral cell state and charged cell state. In the later, one electron was added to the supercell to compensate for the difference of the valence

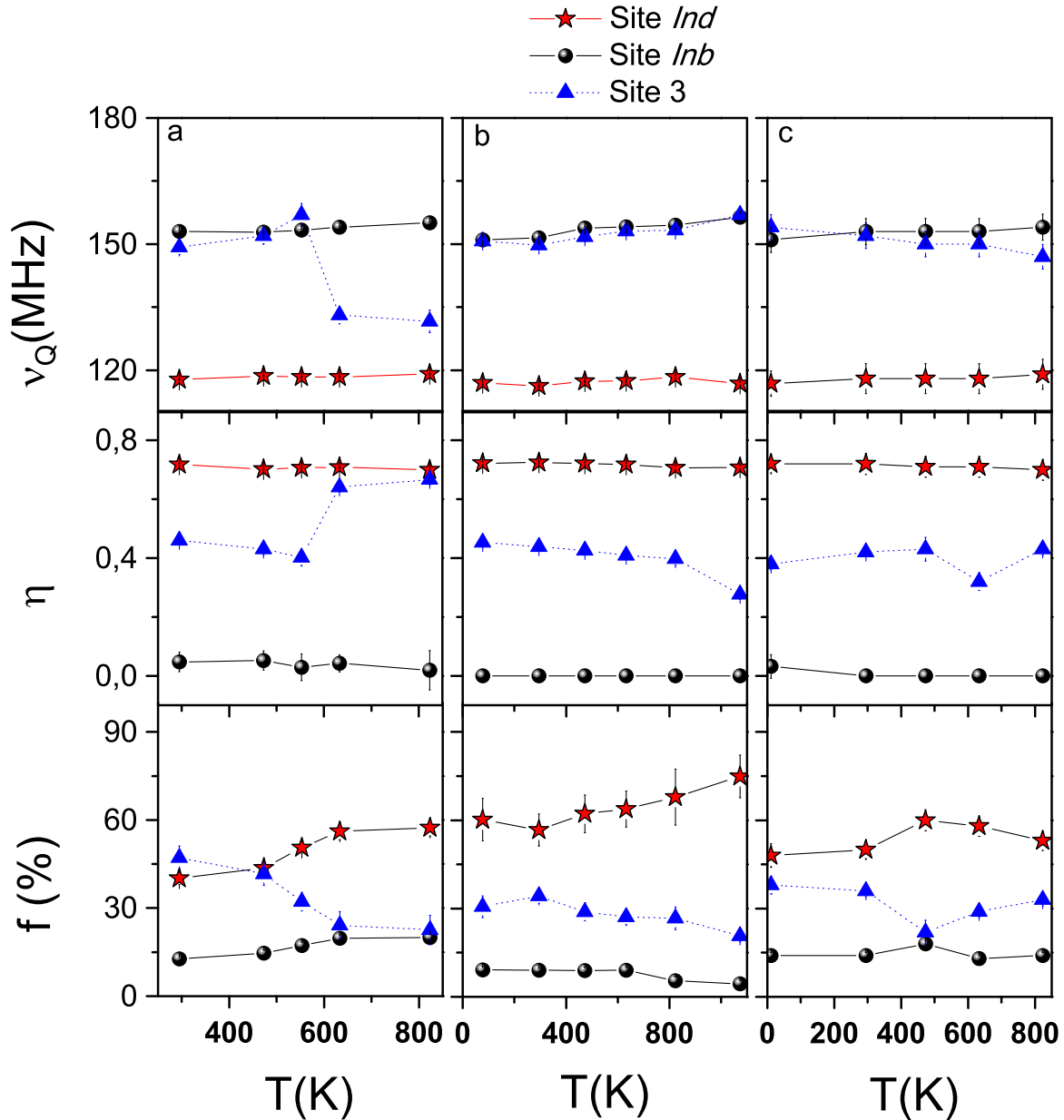


Fig. 5. Temperature dependence of hyperfine parameters: ν_Q , η , and fractional site population f measured at ^{111}Cd impurities in In_2O_3 samples doped with (a) 5% of Co, (b) 5% Fe, and (c) 5% Ni. Data for pure (0%) and 5% Fe doped In_2O_3 samples are from Sena et al. [31].

between Cd^{2+} and In^{3+} . Charged state results are $V_{zz} = +5.72 \times 10^{21} \text{ V/m}^2$ and $\eta = 0.72$ for the Cd located at site *Ind*, and $V_{zz} = +7.68 \times 10^{21} \text{ V/m}^2$ and $\eta = 0.00$ for the Cd impurity located at site *Inb* of the bixbyite structure. Neutral state results are $V_{zz} = -3.08 \times 10^{21} \text{ V/m}^2$ and $\eta = 0.01$ for the Cd located at site *Ind*, and $V_{zz} = +7.15 \times 10^{21} \text{ V/m}^2$ and $\eta = 0.00$ for the Cd impurity located at site *Inb*. Experimental PAC results at room temperature for pure In_2O_3 produce $V_{zz} = 5.83 \times 10^{21} \text{ V/m}^2$ ($\nu_{Qd} = 117 \text{ MHz}$ and $\eta_d = 0.72$) and $V_{zz} = 7.57 \times 10^{21} \text{ V/m}^2$ ($\nu_{Qb} = 152 \text{ MHz}$ and $\eta_b = 0.00$), respectively for sites *Ind* and *Inb*. The comparison of these results with the calculated values leads us to conclude that the charge state of the site *Ind* is negative, whereas it can be ambiguous for site *Inb* since both charge states give almost the same results for V_{zz} and η . Nevertheless, one can assume that the charge state should be negative for both the sites since there is not a known reason for them to have different behavior in this respect. One can also say that the WC-APW+lo method produces a very good agreement with the experimental hyperfine parameters for pure

In_2O_3 .

In order to obtain a more realistic simulation of the hyperfine parameters in TM-doped In_2O_3 , which can be better compared with experimental results, we performed DFT calculations in a supercell of In_2O_3 where two In atoms were replaced by one Cd and one Fe atom as a second nearest neighbor from each other (six oxygen atoms are always the first nearest neighbors of each cationic site). Three possible situations were considered: Cd at site *Inb* and Fe at site *Ind* (Cd@b-Fe@d), Cd at site *Ind* and Fe at site *Inb* (Cd@d-Fe@b) or at site *Inb* (Cd@d-Fe@b). Results of these calculations are shown in Table 3.

The values of the calculated V_{zz} and η shown in Table 3 must be compared with those for the pure In_2O_3 :Cd ($V_{zz} = +5.72 \times 10^{21} \text{ V/m}^2$ and $\eta = 0.72$ for the Cd located at site *Ind*, and $V_{zz} = +7.68 \times 10^{21} \text{ V/m}^2$ and $\eta = 0.00$ for the Cd impurity located at site *Inb*) in the charged state. When Cd@b-Fe@d results are compared with results for Cd@b in pure In_2O_3 :Cd, one notices only a small change in V_{zz} , from 7.68 to 7.99 (in 10^{21} V/m^2 units) and η

Table 2

Room temperature hyperfine parameters obtained from the fitted PAC spectra of pure as well as 5% TM-doped In_2O_3 (TM = Fe, Co and Ni) samples. Data for pure (0%) and 5% Fe doped In_2O_3 samples are from Sena et al. [31].

TM	$f(\%)$	ν_Q (MHz)	η	δ
Site <i>Ind</i>				
0%	75 ± 5	117 ± 1	0.72 ± 0.01	0.029 ± 0.002
5% Fe	57 ± 3	116 ± 1	0.72 ± 0.01	0.048 ± 0.001
5% Co	40 ± 4	118 ± 1	0.72 ± 0.01	0.025 ± 0.001
5% Ni	43 ± 4	118 ± 1	0.72 ± 0.01	0.030 ± 0.002
Site <i>Inb</i>				
0%	25 ± 2	152 ± 1	0	0.010 ± 0.003
5% Fe	9 ± 1	151 ± 1	0	0.013 ± 0.003
5% Co	13 ± 1	153 ± 1	0	0.008 ± 0.003
5% Ni	12 ± 1	152 ± 1	0	0.010 ± 0.003
Site 3				
0%	–	–	–	–
5% Fe	34 ± 2	150 ± 1	0.44 ± 0.01	0.109 ± 0.005
5% Co	47 ± 3	149 ± 2	0.46 ± 0.02	0.164 ± 0.007
5% Ni	45 ± 5	154 ± 3	0.43 ± 0.02	0.154 ± 0.011

Table 3

Hyperfine parameters V_{zz} and η for three possible situations where Cd and Fe impurities occupy cation sites as second nearest neighbors in In_2O_3 unit cell as calculated with the APW+lo method in the PBE-GGA approximation with a dilution of 1:32 (3%). In all these cases, the unit cell had 80 atoms, the calculations were spin-polarized and all the forces on atoms were minimized without symmetry constraints. Experimental values are also displayed.

Supercell configuration	Charge state	V_{zz} ($\times 10^{21}$ V/m ²)	η
Cd@b–Fe@d	Neutral	8.39	0.16
	Charged	7.99	0.20
Cd@d–Fe@d	Neutral	7.37	0.59
	Charged	5.28	0.77
Cd@d–Fe@b	Neutral	9.36	0.55
	Charged	8.19	0.57
Experimental	Site <i>Ind</i>	5.78	0.72
	Site <i>Inb</i>	7.52	0.00
	Site 3	7.57	0.44

from zero to 0.20 (the presence of the TM impurity as a second nearest neighbor of Cd breaks the axial symmetry). Therefore, it can be concluded that the presence of one Fe atom near the Cd probe provokes only a minor change on the Cd hyperfine parameters. The same is true if one compares results for Cd@d–Fe@d with those for Cd@d in pure In_2O_3 :Cd. The only situation where a larger change occurs is for Cd@d–Fe@b when compared with the Cd@d in pure In_2O_3 :Cd. In this situation, the V_{zz} value (in 10^{21} V/m² units) changes from 5.72 to 8.19 and becomes close to the value for Cd@b in pure In_2O_3 :Cd. Analogously, the η value changes from 0.72 to 0.57. This configuration will then present a V_{zz} value similar to that for the site *Inb* in pure In_2O_3 :Cd but with a distinct η value. In this way, the configuration Cd@d–Fe@b does not have any counterpart in the pure In_2O_3 :Cd and will then be experimentally seen as an extra site (site 3) in addition to the two sites *Inb* and C of the pure In_2O_3 :Cd. The experimental observations corroborate this hypothesis very well. Interestingly, the case Cd@d–Fe@d, neutral cell, also fits well with the site 3. We speculate that this case is unlikely to occur because of its charge neutrality and is in contradiction to the findings with the pure In_2O_3 :Cd. Therefore, we concluded that the additional site (site 3) experimentally observed corresponds to Cd probes at sites *Ind* with Fe atoms as the second nearest neighbor at sites *Inb*. This conclusion agrees with results of calculations presented in Section 4.1 (see Table 1), which show that the configuration where TM impurities are at site *Inb* is more stable (lower E_{min}) than that where TM are at sites *Ind*. The preference of TM to occupy sites *Inb* in In_2O_3 structure was also

experimentally verified by X-ray and neutron diffraction measurements in In_2O_3 doped with Cr [46].

With regard to the populations of the sites, one notices that the population of the sites *Inb*, when In_2O_3 is doped with Fe, decrease in comparison with the pure In_2O_3 :Cd, from 25% to 9% (see Table 2). Part of this effect could be explained by the fact that the Cd@b site is also affected by the presence of the neighbor Fe@d, resembling then the site 3. Thus, in the fit process, part of the site *Inb* fraction moves to the site 3 fraction. The fraction analysis will be better discussed in the next subsection.

4.4. Magnetization interpretation

The magnetic behavior as well as its origin in semiconductor oxides doped with transition metals is currently of great interest mainly because contradictory results have been reported. Although ferromagnetic behavior has been observed, it is believed, based on experimental evidences, that TM ions contribute only with a paramagnetic behavior [12,13]. Magnetization (M) as a function of the applied field (H) curves for the 5% TM-doped In_2O_3 samples (TM = Fe, Co and Ni) measured at room temperature and at 5 K is shown in Fig. 6a and c, respectively. A visual inspection of the M vs. H curves indicates a paramagnetic behavior for the Ni- and Co-doped In_2O_3 , and a ferromagnetic response which coexists with a paramagnetic response for the Fe-doped In_2O_3 . After subtracting the paramagnetic contribution from the M vs. H curves of TM-doped In_2O_3 samples, it is possible to clearly observe a weak ferromagnetic signal with very low saturation magnetization (M_s) values, as shown in Fig. 6b. The Fe-doped In_2O_3 sample shows a $M_s = 22.1 \times 10^{-3}$ emu/g, while Ni and Co-doped In_2O_3 samples show much smaller values: $M_s = 1.8 \times 10^{-3}$ emu/g and $M_s = 1.5 \times 10^{-3}$ emu/g, respectively.

The M vs. H curves at 5 K are also displayed in Fig. 6c, which are well represented by the Brillouin function (solid lines in the figure) in the region of high applied fields. We emphasize that for low applied fields, the magnetization curves show magnetic hysteresis. Fig. 6d shows the DC magnetic susceptibility (χ) as a function of the temperature obtained in an applied field of 5 kOe for all samples. The observed behavior can be well described by the Curie–Weiss law given by $\chi = \chi_0 + C/(T - \theta)$ and the resulting parameters are shown in Table 4. We would like to call attention to the negative sign of θ that suggests the occurrence of anti-ferromagnetic interactions between the magnetic ions in the paramagnetic phase. Although values of μ_{eff} for Co and Ni showed much smaller values when compared to the experimental value of the effective magnetic moment of Co^{2+} and Ni^{2+} ($\mu_{\text{eff}} = 4.90\mu_B$ and $\mu_{\text{eff}} = 3.12\mu_B$, respectively [47]), they are quite compatible with the saturation magnetic moment of Co^{2+} in cobalt oxide (CoO) and Ni^{2+} in nickel oxide (NiO), $3.35\text{--}3.98\mu_B$ [48] and $1.9\mu_B$ [49], respectively. Results from spin-polarized DFT calculations for Fe, Co, and Ni at D sites of In_2O_3 give the magnetic moment at the TM impurity (in μ_B), respectively, as 3.89, 2.96 and 0.79. Although the absolute values are smaller than the experimental ones, which is a characteristic of the calculation method, the same systematic observed in experimental measurements is preserved. The value of the effective magnetic moment of iron ions in Fe-doped In_2O_3 may suggest that Fe ions act with +2 valence when compared to the experimental values of $\mu_{\text{eff}} = 5.36\mu_B$ for Fe^{2+} and $\mu_{\text{eff}} = 5.82\mu_B$ for Fe^{3+} reported by Blundell [47]. It also seems to be consistent with the saturation magnetization of Fe^{2+} in iron oxide (FeO), where $\mu = 3.32\text{--}4.2\mu_B$ [48]. It is worth mentioning that smaller magnetic moments are expected when superexchange antiferromagnetic (AFM) coupling occurs, since, for instance, AFM pairs make no net contributions and triplets contribute with 1/3 of the magnetic moment. We, therefore, conclude that Co and Ni ions present

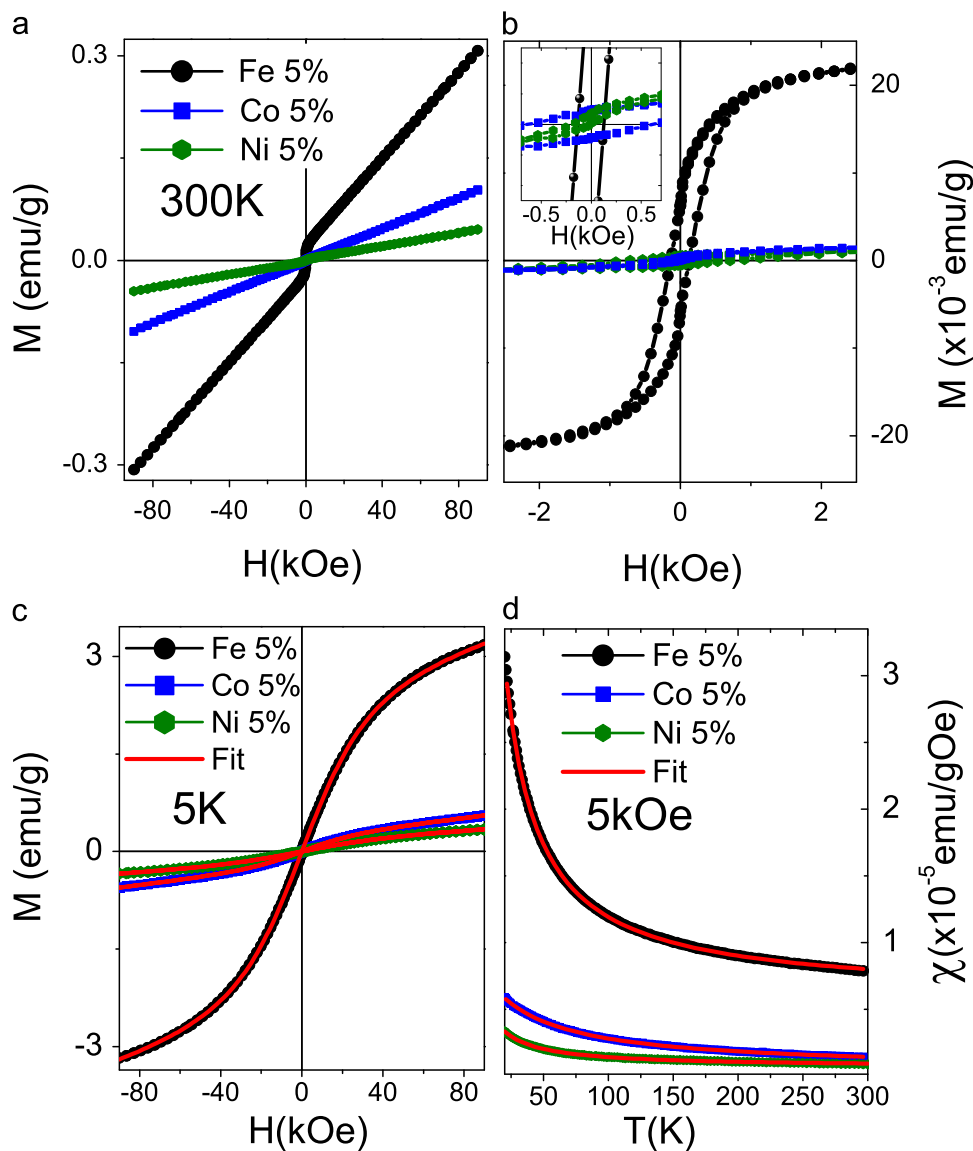


Fig. 6. (a) Magnetization (M) as a function of the applied magnetic field (H) at 300 K. (b) M vs. H curves after subtracting the paramagnetic contribution. (c) M vs. H curves at 5 K, the solid lines represent the fit to the Brillouin function. (d) DC magnetic susceptibility (χ) as a function of temperature where the solid lines represent the fit to the Curie-Weiss law.

Table 4

Magnetic parameters obtained from the fit of the Curie-Weiss function to the data. μ_{eff} is the effective magnetic moment, C is the Curie constant, χ_0 is a temperature-independent susceptibility and θ is the Curie-Weiss temperature.

TM	C (emu/gOeK)	μ_{eff} (μ_B)	χ_0 (emu/gOe)	θ (K)
Fe	6.3×10^{-4}	5.21 ± 0.04	5.9×10^{-6}	-5.0 ± 0.1
Co	3.3×10^{-4}	3.77 ± 0.06	4.6×10^{-7}	-41.9 ± 0.4
Ni	0.8×10^{-4}	1.86 ± 0.11	6.6×10^{-7}	-11.3 ± 0.4

valence +2 when incorporated to In_2O_3 and that there is a high possibility that Fe ions have +2 valence as well.

If the ferromagnetism is present in the samples and if it is not due to clusters of metallic or oxide phases of TM, an intriguing question is raised: Why a sensitive technique such as PAC spectroscopy did not detect it? A possible direct answer to this question would be that the magnetism in TM-doped In_2O_3 is not conventional, i.e. it is not originated from the coupling of localized magnetic moments at TM ions otherwise it would be detected in all sites of samples. Nevertheless, it is possible to look for some

characteristics in PAC spectra that could be an evidence of magnetism. In fact, site fraction 3 presents large quadrupole frequency distribution (δ 11–16%). The effect of a broad δ on the PAC spectra is a decrease in the amplitudes of spectra with time. However, the same effect can be obtained if a weak magnetic interaction is added to a strong quadrupole interaction as reported in PAC measurements with ^{111}Cd at In sites in CeIn_3 [50,51]. Therefore, site fraction 3 can also be fitted using a combined interaction by adding a magnetic dipole frequency to the electric quadrupole frequency instead of a pure quadrupole interaction with a wide frequency distribution. This procedure was reported before when PAC data on ^{181}Ta in HfO_2 nanoparticles, which was characterized by a quadrupole interaction with the expected quadrupole frequency and asymmetry parameter plus a second frequency with a wide distribution [52], has been re-analyzed. In this new analysis, the second wide distributed quadrupole frequency was fitted by a combination of well-defined electric quadrupole plus magnetic dipole frequencies and the results supported by *ab initio* DFT calculations [53].

In order to search for magnetic interactions, PAC spectra were

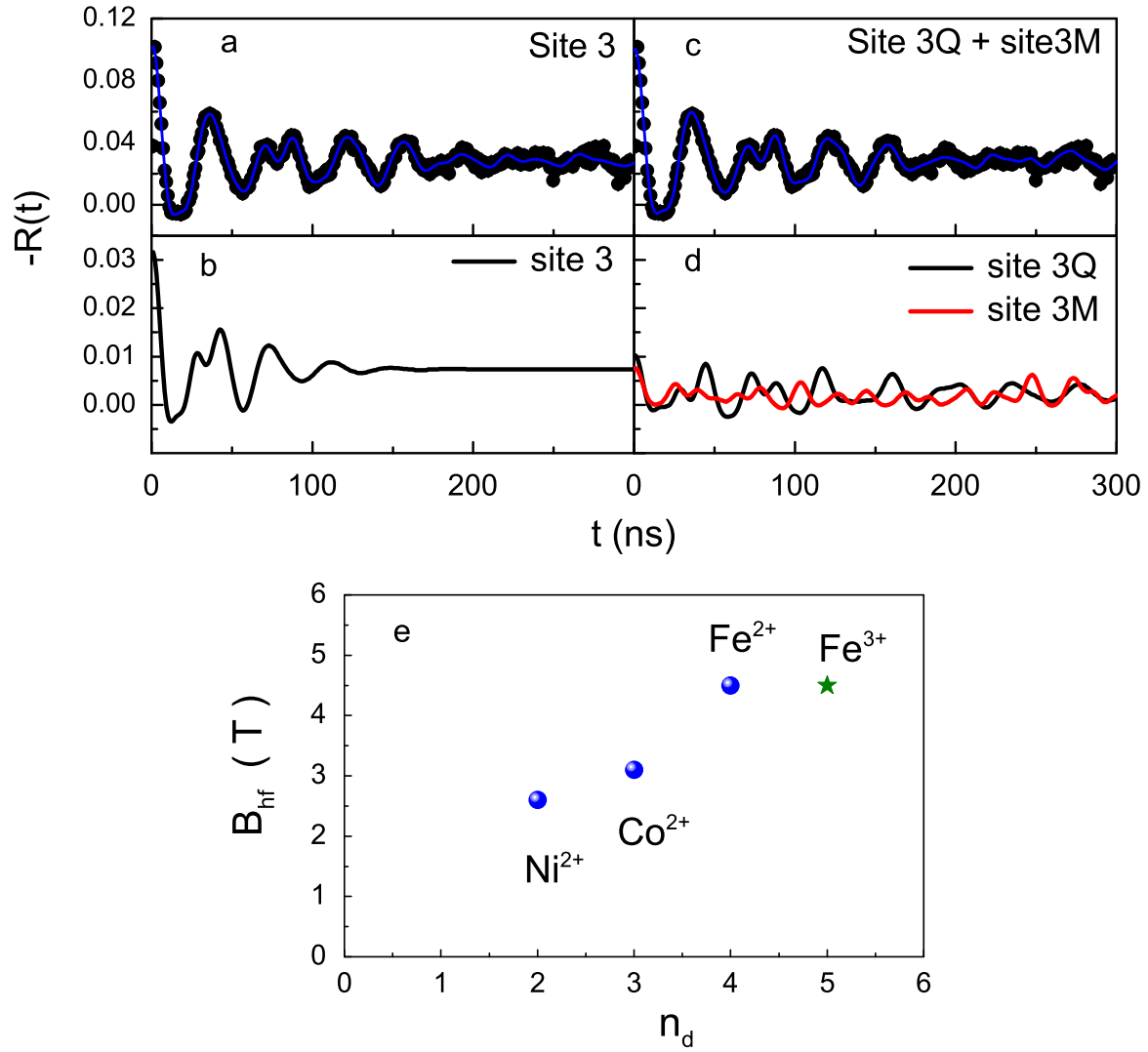


Fig. 7. PAC spectra measured at ^{111}Cd in Fe-doped In_2O_3 at room temperature fitted with: (a) three pure electric quadrupole site fractions: two inequivalent site fractions C and D plus a third site (site 3) characterized by a broad distributed quadrupole frequency shown in (b), and (c) two electric quadrupole fractions (site Ind and Inb) plus two site fractions characterized by well-defined electric quadrupole (site 3Q) and magnetic dipole (site 3M) frequencies showed in (d). (e) Magnetic hyperfine field at ^{111}Cd in TM-doped In_2O_3 as a function of the number of unpaired d electrons for the TM ion (n_d).

Table 5

Hyperfine parameters including a magnetic dipole interaction, characterized by a dipole magnetic frequency (ν_M), obtained from the fit to room temperature PAC spectra of 5% TM-doped In_2O_3 (TM=Fe,Co and Ni) samples.

TM	f (%)	ν_Q (MHz)	η	δ	ω_L (Mrad/s)	B_{hf} (T)
Site Ind						
Fe	68 ± 2	116 ± 1	0.74 ± 0.01	0.050 ± 0.001	–	–
Co	51 ± 2	117 ± 1	0.73 ± 0.01	0.025 ± 0.001	–	–
Ni	66 ± 1	117 ± 1	0.73 ± 0.01	0.042 ± 0.001	–	–
Site Inb						
Fe	14 ± 1	152 ± 1	0	0.017 ± 0.002	–	–
Co	21 ± 1	153 ± 1	0	0.014 ± 0.004	–	–
Ni	17 ± 1	152 ± 1	0	0.015 ± 0.002	–	–
Site 3Q						
Fe	11 ± 1	149 ± 1	0.37 ± 0.01	0.028 ± 0.004	–	–
Co	21 ± 3	133 ± 1	0.61 ± 0.01	0.068 ± 0.007	–	–
Ni	10 ± 5	155 ± 1	0.31 ± 0.01	0.017 ± 0.003	–	–
Site 3M						
Fe	7 ± 1	128 ± 1	0.14 ± 0.01	0	65.3 ± 0.5	4.6 ± 0.1
Co	7 ± 1	127 ± 1	0.22 ± 0.01	0	45.9 ± 0.4	3.1 ± 0.1
Ni	7 ± 1	150 ± 1	0.43 ± 0.01	0	37.7 ± 0.4	2.6 ± 0.1

re-analyzed considering a combined electric quadrupole plus magnetic dipole interaction for site fraction 3. The best fit was achieved when site 3 was split in two parts: a fraction characterized by a pure electric quadrupole interaction (site 3Q) with parameters similar to those obtained in the previous fit and a fraction characterized by a combined interaction (site 3M). Comparison between previous and new fit is shown in Fig. 7 and the results of new fit to room-temperature spectra are displayed in Table 5. The fit of a theoretical model to PAC spectra is quite sensitive and often has an alternative possibility for the used model, especially if more site fractions are added. It is, therefore, important to show the possible different theoretical models when the PAC spectra admit ambiguous fit. The most probable model is that which describes more realistically the observed phenomenon.

Results of the new fit show very similar values of hyperfine parameters for sites *Ind* and *Inb* except for fractional site populations, which for site *Ind* of all compounds are closer to the expected value of 75% than in the previous fit. Cd probes at sites 3M detected a magnetic interaction, which indicates the presence of a magnetic TM atom in their neighborhood. As discussed in Section 4.3, the most probable configuration for the extra site 3 is Cd at sites *Ind* and TM at sites *Inb*. Considering, therefore, this configuration for sites 3M, we found that the total fractional site population of Cd at sites *Ind* in Fe-doped samples is 75% as expected. The value for Ni-doped samples is 73%, but for Co-doped samples this value is only 58%. The values for ν_Q and η for sites 3M are quite different from those observed for regular sites *Ind*. This difference is due to a defect in the nearest neighborhood of Cd probes, probably an oxygen vacancy as will be discussed below. The observed sites 3Q were then assigned to Cd probes at sites *Inb* but with a defect nearby, because of the non-zero η values. As a consequence, the total fractional site population of sites *Inb* for Fe- and Ni-doped samples are 25% and 27%, respectively as expected. The value for Co-doped samples is 42%, much higher than the awaited value. However, ν_Q and η values are between the values for regular sites *Ind* (117 MHz and 0.73, respectively) and the average values for site 3Q observed for Fe- and Ni-doped samples (~152 MHz and ~0.34, respectively). As the frequency distribution for Co-doped samples observed at sites 3Q is higher than those for Fe- and Ni-doped samples, we, therefore, suppose that part of the fractional site population for this site is indeed due to Cd probes at regular sites *Ind*, which would bring the observed fractional site populations back to the expected values. Moreover, site 3Q shows quadrupole frequency and asymmetry parameter values for Co-doped samples aligned to those observed in the previous fit at high temperatures, which now rule out the possibility of a totally unexpected structural transition. Furthermore, the presence of magnetism observed by magnetization measurements must be incorporated in the theoretical model used to fit the PAC spectra. Taking into account all these considerations, this fit describes the experimental situation better than the previous one.

The magnetic frequency was observed to decrease when temperature increases for Fe-doped samples: at 77 K ν_M is 11 MHz decreasing to 10.4 MHz and 8 MHz at 295 K and 823 K, respectively, and vanishing at 1073 K. This behavior is a signature of magnetic ordering with a transition temperature higher than 823 K, and according to the population of the site fraction with magnetic interaction, this magnetic interaction is only observed in a small part of the sample and, presumably, it has a local character. Noteworthy, the associated magnetic hyperfine field (B_{hf}) shows increasing values of 2.6 T, 3.1 T, and 4.6 T, respectively for Ni, Co, and Fe. These values present a remarkable almost linear dependence on the number of unpaired d electrons (n_d) of Ni^{2+} ($n_d=2$), Co^{2+} ($n_d=3$), and Fe^{2+} ($n_d=4$) or Fe^{3+} ($n_d=5$), as shown in Fig. 7e. B_{hf} results from DFT calculations are (for neutral and charged unit cell, respectively) 3.0 T and 2.5 T (Cd@b–Fe@d), 3.4 T

and 2.3 T (Cd@d–Fe@d), and 3.9 T and 3.6 T (Cd@d–Fe@b). Spin-polarized DFT calculations, therefore, show that for Fe atom at sites *Inb* the magnetic hyperfine field on Cd positions at next nearest sites *Ind* is 3.6 T for the charged unit cell, which is 21% lower than the experimental value of 4.6 T, showing a very good agreement. In order to rule out the possibility that the observed magnetic hyperfine field at sites 3M is due to secondary phases, results were compared to those for possible TM phases and the values are quite different. For instance, for iron at room temperature, B_{hf} is around 39 T for pure iron, [54] 7.5 T for Fe_2O_3 with an axially symmetric ($\eta=0$) quadrupolar interactions with $\nu_Q=153$ MHz as reported by Asai et al. [55], and around 12 T for Fe_3O_4 oxide [56]. At room temperature, B_{hf} is around 28 T for pure cobalt [57], 6.7 T for pure nickel [58], and 16.5 T for NiO oxide [45].

The experimental results of B_{hf} shows that although the TM ions probably only contribute with a paramagnetic component to the magnetic behavior of the TM-doped In_2O_3 , their *d* band has a strong influence in the magnetic hyperfine field and, consequently, in the magnetic ordering of the compounds. In the case of Fe-doped samples, both Fe^{2+} ($n_d=4$) and Fe^{3+} ($n_d=5$) fit well in the observed behavior in which B_{hf} increases when the number of unpaired d electrons increases. There is a strong evidence that the valence of Fe as a substitutional impurity in In_2O_3 thin films depends on the partial pressure of the oxygen atmosphere and temperature of annealing [59,23]. Therefore, when the partial pressure of oxygen increases Fe^{2+} oxidize to Fe^{3+} increasing the Fe^{3+}/Fe^{2+} ratio [59]. In powder samples prepared at high temperatures in air and subsequently submitted to annealing in vacuum, Fe behaves as a mixture of +2 and +3 valences [29]. There is also a strong indication that the magnetic behavior of In_2O_3 doped with Fe is strongly dependent on the Fe valence: In_2O_3 doped with Fe^{2+} shows ferromagnetic behavior [23] while In_2O_3 doped with Fe^{3+} shows paramagnetic behavior [22]. Admitting that the TM impurities have +2 valence when they replace In^{3+} at sites *Inb* of In_2O_3 , an oxygen vacancy has a fairly high probability to appear as a next nearest neighbor of the TM ion (see Fig. 8). Electrons can be trapped in this oxygen vacancies and act as shallow donors. Our PAC results show, therefore, that only part of the TM-doped In_2O_3 samples is magnetically ordered: that part where ^{111}Cd probes are close to TM-ions at sites *Inb* and possibly close to oxygen vacancies. This possibility is also inferred from the observation that the quadrupole parameters (ν_Q and η) for sites 3M are quite different from those for the regular sites *Ind* and *Inb*, particularly for Fe- and Co-doped samples, showing that the environment around the probes are different, probably due to the oxygen vacancy. Such a situation is more likely to occur in the region near the surface of the grains.

Oxygen vacancies have been pointed out to play an important role in the magnetic behavior of TM-doped In_2O_3 [12,60,61]. Guam et al. [61] reported that with oxygen vacancies as Fe next nearest neighbor in Fe-doped In_2O_3 a weak ferromagnetic ground state was produced. The ferromagnetism in TM-doped semiconductor oxides has been explained by a model in which ferromagnetic indirect exchange interactions are mediated by shallow donor electrons trapped in oxygen vacancies. The 3d electrons of the TM impurities have their spins aligned by this coupling within an expanded orbit. The overlap of neighboring different orbits is able to align a large number of TM ions resulting in a ferromagnetic ordering. Coey et al. [26,27] also reported that TM doping acts as a charge reservoir from which electrons are transferred to vacancies provoking the split of the density of states permitting, as a consequence, TM ions to coexist in different charge states.

5. Conclusion

Bulk samples of semiconductor oxide In_2O_3 doped with Co and

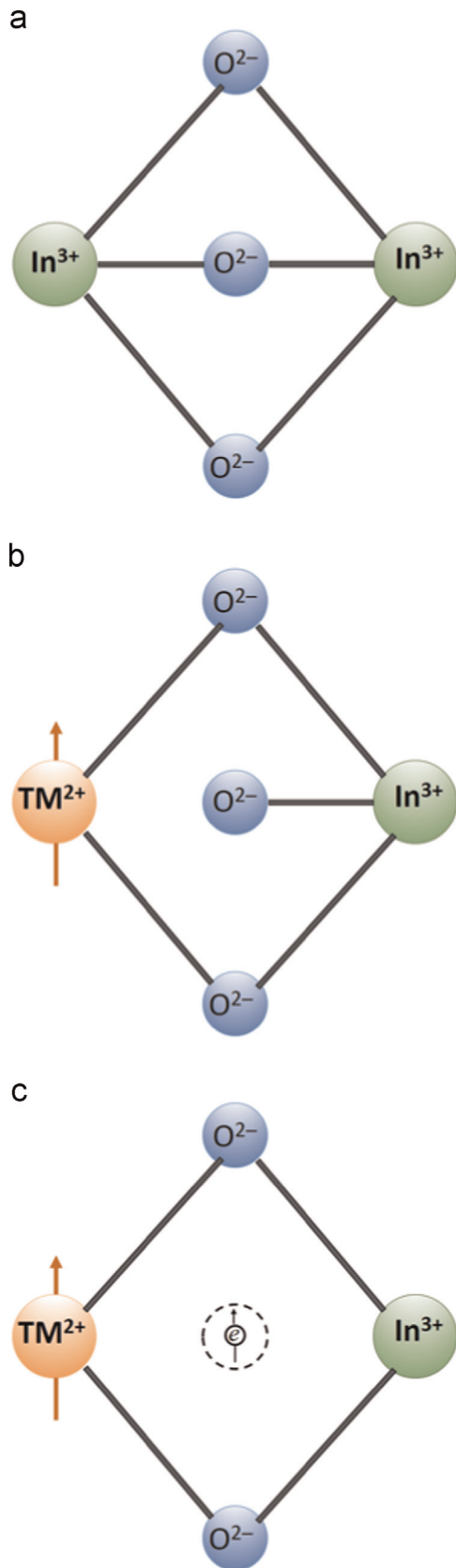


Fig. 8. Schematic diagram of oxygen and cation bounds in In_2O_3 : (a) pure oxide, (b) doped with TM^{2+} ion, and (c) one oxygen vacancy with an electron trapped.

Ni transition metals were prepared by the sol–gel method and had their structure and composition characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). Concentration of TM in the samples was measured by X-ray fluorescence. Room temperature results of magnetization measurements showed that TM-doped In_2O_3 samples are characterized by ferromagnetic ordering which coexists with a paramagnetic contribution. From XRD measurements and APW+lo calculations it was observed a gradual decrease in the lattice parameter when In_2O_3 is doped with Ni, Co, and Fe, which is a strong evidence of the replacement of In by TM ions in the In_2O_3 structure. Moreover, the excellent agreement between calculations and PAC results for In_2O_3 allowed the identification of the three site fractions observed for the TM-doped samples with PAC measurements. An important observation was extracted from PAC spectroscopy and DFT calculation results: transition metal impurities probably prefer to occupy sites Inb of the In_2O_3 crystal structure. PAC results also revealed that only a small part of samples present a fraction with magnetic interactions and B_{hf} on $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ probes at next nearest neighbor of TM sites is 2.6 T, 3.1 T, and 4.6 T, respectively for Ni, Co, and Fe doping. These B_{hf} values show a remarkable linear dependence on the number of unpaired 3d electrons of the transition metal. These results are ascribed to the presence of oxygen vacancies next to the transition metal sites near the surface of the particles. As the particles in bulk samples are big, the surface area/volume of particles is much smaller in bulk samples than in thin films for which the influence of surface is stronger and the observed magnetism is more intense. The dilute doping of transition metal ions in semiconductor oxides causes unconventional magnetic phenomena at an atomic scale, which opens a new frontier in the physics of magnetism. The identification of the origin as well as the correct description of such magnetic phenomena is extremely important to expand the fundamental knowledge of the physics of magnetism and will consequently have huge impact in the technological applications of these materials.

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References

- [1] J.H. Lee, *Sens. Actuat. B* 140 (2009) 319.
- [2] E. Fortunato, P. Barquinha, R. Martins, *Adv. Mater.* 24 (2012) 2945.
- [3] T. Minami, *Semicond. Sci. Technol.* 20 (2005) S35.
- [4] B.T. Matthias, R.M. Bozorth, J.H. Van Vleck, *Phys. Rev. Lett.* 7 (1961) 160.
- [5] H. Ohno, H. Munekata, T. Penney, S. von Molnar, L.L. Chang, *Phys. Rev. Lett.* 68 (1992) 2664.
- [6] H. Ohno, *Science* 281 (1998) 951.
- [7] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* 287 (2000) 1019.
- [8] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, Shin-ya Koshihara, H. Koinuma, *Science* 291 (2001) 854.
- [9] A. Ney, K. Ollefs, S. Ye, T. Kammermeier, V. Ney, T.C. Kaspar, S.A. Chambers, F. Wilhelm, A. Rogalev, *Phys. Rev. Lett.* 100 (2008) 157201.
- [10] G. Ciatto, A. Di Trollo, E. Fonda, P. Alippi, A.M. Testa, A.A. Bonapasta, *Phys. Rev. Lett.* 107 (2011) 127206.
- [11] D. Berardan, E. Guilmeau, D. Pelloquin, J. Magn. Magn. Mater. 320 (2008) 983.
- [12] A.M.H.R. Hakimi, M.G. Blamire, S.M. Heald, M.S. Alshammari, M.S. Alqahtani, D.S. Score, H.J. Blythe, A.M. Fox, G.A. Gehring, *Phys. Rev. B* 84 (2011) 085201.
- [13] E. Pellicer, M. Cabo, E. Rossinyol, P. Solsona, S. Suri nach, M.D. Baró, J. Sort, *Adv. Funct. Mater.* 23 (2013) 900.
- [14] D.H. Kim, J.S. Yang, K.W. Lee, S.D. Bu, T.W. Noh, S.J. Oh, Y.W. Kim, J.S. Chung, H. Tanaka, H.Y. Lee, T. Kawai, *Appl. Phys. Lett.* 81 (2002) 2421.

- [15] F. Golmar, M. Villafuerte, A. Mudarra Navarro, C.E. Rodríguez Torres, J. Barzola-Quiquia, P. Esquinazi, S.P. Heluani, J. Mater. Sci. 45 (2010) 6174.
- [16] D. Bérardan, E. Guilmeau, J. Phys.: Condens. Matter 19 (2007) 236224.
- [17] M.A. García, E. Fernández Pinel, J. De la Venta, A. Quesada, V. Bouzas, J. F. Fernández, J.J. Romero, M.S. Martín-González, J.L. Costa-Kramer, J. Appl. Phys. 105 (2009) 013925.
- [18] R. Lardé, E. Talbot, F. Vurpillot, P. Pareige, G. Schmerber, E. Beaurepaire, A. Dinia, V. Pierron-Bohnes, J. Appl. Phys. 105 (2009) 126107.
- [19] A. Di Trollo, R. Larciprete, S. Turchini, N. Zema, Appl. Phys. Lett. 97 (2010) 052505.
- [20] A.M.H.R. Hakimi, F. Schoofs, R. Bali, N.A. Stelmashenko, M.G. Blamire, S. Langridge, S.A. Cavill, G. van der Laan, S.S. Dhesi, Phys. Rev. B 82 (2010) 144429.
- [21] S.S. Farvid, M. Hedge, P.V. Radovanovic, Chem. Mater. 25 (2013) 233.
- [22] C. Fahed, S.B. Qadri, H. Kim, A. Piqué, M. Miller, N.A. Mahadi, M.V. Rao, M. Osofsky, Phys. Status Solidi C 7 (2010) 2298.
- [23] Xiao-Hong Xu, Feng-Xian Jiang, Jun Zhang, Xiao-Chen Fan, Hai-Shun Wu, G. A. Gehring, Appl. Phys. Lett. 94 (2009) 212510.
- [24] P. Kharel, C. Sudakar, M.B. Sahana, G. Lawes, R. Suryanarayanan, R. Naik, V. M. Naik, J. Appl. Phys. 101 (2007) 09H117.
- [25] B.B. Straumal, A.A. Mazilkin, S.G. Protasova, A.A. Myatiev, P.B. Straumal, G. Sch'utzu, P.A. van Aken, E. Goering, B. Baretzky, Phys. Rev. B 79 (2009) 205206.
- [26] J.M.D. Coey, M. Venkatesan, C.B. Fitzgerald, Nat. Mater. 4 (2005) 173.
- [27] J.M.D. Coey, K. Wongsaprom, J. Alaria, M. Venkatesan, J. Phys. D: Appl. Phys. 41 (2008) 134012.
- [28] J. Philip, A. Punnoose, B.I. Kim, K.M. Reddy, S. Layne, J.O. Holmes, B. Satpati, P. R. Leclair, T.S. Santos, J.S. Moodera, Nat. Mater. 5 (2006) 298.
- [29] F.-X. Jiang, X.-H. Xu, J. Zhang, H.-S. Wua, G.A. Gehring, Appl. Surf. Sci. 255 (2009) 3655.
- [30] S. Heald, M.S. Alshammari, S. Alfehaid, M. Alotaibi, Qi Feng, A.M.H.R. Hakimi, J. Phys.: Conf. Ser. 430 (2013) 012081.
- [31] C. Sena, M.S. Costa, G.A. Cabrera-Pasca, R.N. Saxena, A.W. Carbonari, Hyperf. Interact. 221 (2013) 105.
- [32] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, WIEN2k: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, Technische Universität Wien, Austria, 2001, ISBN: 3-9501031-1-2.
- [33] G.K.H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, L. Nordström, Phys. Rev. B 64 (2001) 195134.
- [34] W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1133.
- [35] Z. Wu, R.E. Cohen, Phys. Rev. B 73 (2006) 235116.
- [36] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [37] G.N. Darriba, L.A. Errico, P.D. Eversheim, G. Fabricius, M. Rentería, Phys. Rev. B 79 (2009) 115213.
- [38] D. Richard, E.L. Muñoz, T. Butz, L.A. Errico, M. Rentería, Phys. Rev. B 82 (2010) 035206.
- [39] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.
- [40] Ch.Y. Wang, V. Cimalla, H. Romanus, Th. Kups, G. Ecke, Th. Stauden, M. Ali, V. Lebedev, J. Pezoldt, O. Ambacher, Appl. Phys. Lett. 89 (2006) 011904.
- [41] D. Yamashita, T. Yoshioka, S. Nishida, T. Yamamoto, Physica B 407 (2012) 4485.
- [42] R. Dogra, A.C. Junqueira, R.N. Saxena, A.W. Carbonari, J. Mestnik-Filho, M. Moralles, Phys. Rev. B 63 (2001) 224104.
- [43] G.A. Cabrera-Pasca, A.W. Carbonari, B. Bosch-Santos, J. Mestnik-Filho, R. N. Saxena, J. Phys.: Condens. Matter 24 (2012) 416002.
- [44] A.G. Bibiloni, J. Desimoni, C.P. Massolo, L. Mendoza-Zélis, A.F. Pasquevich, F. H. Sánchez, A. López-García, Phys. Rev. B 29 (1984) 1109.
- [45] W. Bolse, M. Uhrmacher, K.P. Lieb, Phys. Rev. B 36 (1987) 1818.
- [46] L. Bizo, M. Allix, H. Niu, M.J. Rosseinsky, Adv. Funct. Mater. 18 (2008) 777.
- [47] S. Blundell, Magnetism in Condensed Matter, first ed., Oxford University Press, New York, 2001.
- [48] F. Tran, P. Blaha, K. Schwarz, P. Novák, Phys. Rev. B 74 (2006) 155108 (and references therein).
- [49] A.K. Cheetham, D.A.O. Hope, Phys. Rev. B 27 (1983) 6964.
- [50] A.W. Carbonari, J. Mestnik-Filho, R.N. Saxena, H. Saitovitch, Hyperfine Interact. 133 (2001) 77.
- [51] G.A. Cabrera-Pasca, J. Mestnik-Filho, A.W. Carbonari, R.N. Saxena, J. Appl. Phys. 113 (2013) 17E133.
- [52] M. Forker, P. de la Presa, W. Hoffbauer, S. Schlabach, M. Bruns, D.V. Szabó, Phys. Rev. B 77 (2008) 054108.
- [53] M.A. Taylor, R.E. Alonso, L.A. Errico, A. Lopez-Garcia, P. de la Presa, A. Svane, N. E. Christensen, Phys. Rev. B 82 (2010) 165203.
- [54] J. Golczewski, K. Maier, Nucl. Instr. Methods Phys. Res. A 244 (1986) 509.
- [55] K. Asai, F. Ambe, S. Ambe, T. Okada, H. Sekizawa, Phys. Rev. B 41 (1990) 6124.
- [56] Z. Inglot, D. Wiarda, K.P. Lieb, T. Wenzel, M. Uhrmacher, J. Phys.: Condens. Matter 3 (1991) 4569.
- [57] B. Lindgren, S. Bedi, R. Wappling, Phys. Scr. 18 (1978) 26.
- [58] W.-D. Zeitz, R. Dogra, A.P. Byrne, S.K. Shrestha, A.V.J. Edge, H. Timmers, Phys. Rev. B 78 (2008) 014406.
- [59] Z.G. Yu, Jun He, Shifa Xu, Qizhen Xue, O.M.J. vant Erve, B.T. Jonker, M. A. Marcus, Young K. Yoo, Shifan Cheng, Xiao-dong Xiang, Phys. Rev. B 74 (2006) 165321.
- [60] S.J. Hu, S.S. Yan, X.L. Lin, X.X. Yao, Y.X. Chen, G.L. Liu, L.M. Mei, Appl. Phys. Lett. 91 (2007) 262514.
- [61] L.X. Guan, J.G. Tao, Z.R. Xiao, B.C. Zhao, X.F. Fan, C.H.A. Huan, J.L. Kuo, L. Wang, Phys. Rev. B 79 (2009) 184412.