Fe impurities in Cd and Zn hosts: Theory and experiment

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In this work we have used the vapor condensation technique to prepare thin Zn and Cd films with low concentrations of ^{57}Fe (0.5 at. %). The films were obtained at 16 K and 300 K and studied by *in situ* Mössbauer spectroscopy and resistivity measurements. The *in situ* Mössbauer spectra, measured at 7 K for the as-prepared films, show that the Fe impurities in the Cd and Zn films mainly occupy lattice sites and have isomer shift values of 0.70 mm/s and 0.53 mm/s, respectively. While for Fe in Zn the isomer shift value agrees well with those in the literature, the value for Fe in Cd is significantly larger than the value previously reported. First-principles calculations of the isomer shift values for Fe impurities on substitutional sites in Zn and Cd, respectively, agree quite well with the experimentally found values.

I. INTRODUCTION

Owing to advances in sample preparation and experimental techniques, it is now possible to investigate the behavior of impurities in metals throughout the periodic table. In particular, for the case of ^{57}Fe impurities, the method of electrodeposition of ^{57}Co was used in the first experiments.[1] Most information regarding impurities in nonalloying systems has been produced and investigated by recoil implantation techniques, combined with online time-differential perturbed angular distributions (TDPAD)[2] and in-beam Mössbauer spectroscopy (IBMS).[3] In the present work we use a different technique, namely vapor condensation, to introduce low concentrations of ^{57}Fe (0.5 at. %) into Zn and Cd. Fe is immiscible in both Cd and Zn (Ref. 4) in this concentration range. The samples were then studied by *in situ* Mössbauer spectroscopy and *in situ* resistivity measurements. Since it is known that fast diffusers have generally very low solubility,[5] we have also investigated the diffusion of iron in Cd and Zn, following the approach of our recent works in the Fe:*Pb*, Fe:*Yb*,[6] and Fe:*Ag* immiscible systems.[7]

The isomer shift (IS) of Fe, as measured by Mössbauer effect, is sensitive to the local charge density at the nuclear position and provides information about the local surroundings of the impurity. The volume occupied by the Fe impurity in the host is one of the factors that can affect the IS, which can actually be used to distinguishing between substitutional and interstitial impurity sites.[8] First-principles calculations have been used to obtain trends for the IS of Fe impurities in several metallic hosts across the periodic table.[9] The results, which in general agree well with experiment, can be understood in terms of a simple model which expresses the charge densities in terms of the number of 4*s* electrons around the Fe impurity, multiplied by the probability of finding one of these electrons at the nucleus. In Fig. 1 we show (black squares) the theoretical IS values calculated by Terrazos and Frota-Pessôa.[9] for substitutional Fe impurities in several metallic hosts across the periodic table. The hosts to the left of Fe are shown in Fig. 1(a), while those to the right of Fe (including Zn and Cd) are shown in Fig. 1(b). Existing experimental IS values for Fe in all the systems are

also shown (empty circles) for comparison. We note that for the simple metal hosts in Fig. 1(b), the experimental values for the IS of Fe are systematically larger than the theoretical ones. The one noticeable exception is Cd, and this suggests that the experimental value of the IS for Fe in Cd shown in the figure may be too low.

To the best of our knowledge, up to now, the only Mössbauer studies of dilute iron impurities in Cd (Ref. 1) and Zn (Refs. 1 and 10) were made with ^{57}Co embedded by electroplating and diffusing at high temperature. Zn and Cd have a high vapor pressure and similar low melting points, 692 K and 594 K respectively, and annealing at high temperature could lead to Cd or Zn sublimation, favoring the formation of small iron clusters[10] and some iron-rich alloys as the Γ_2 phase.[10] In this work, we use the Mössbauer spectra (MS) to obtain the IS values of Fe in Cd and Zn. We also perform slightly more accurate first-principles calculations of the IS in these systems. A comparison between theory, our experimental values, and those in the literature leads to a better understanding of the problem and contributes to the determi-
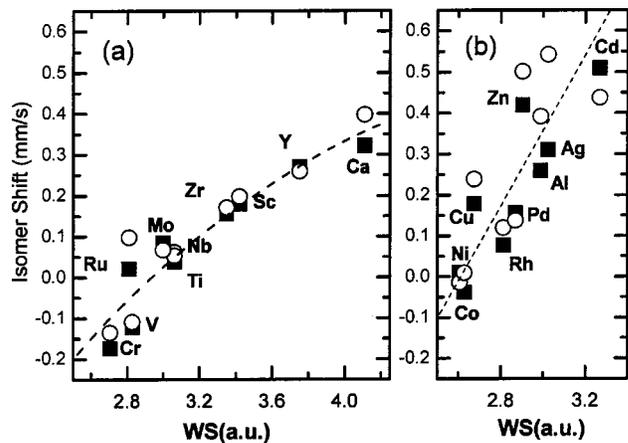

FIG. 1. Isomer shift values for substitutional Fe impurities in several hosts to the left and right of Fe in the periodic table. Experimental (open circles) and theoretical (filled squares) results are given as in Ref. 9.

68 094430-1

nation of more reliable values for the IS of Fe impurities in Cd and Zn.

II. EXPERIMENTAL PROCEDURE

Cd and Zn display strong disparities in size relative to Fe, with volumes per atom which are 85% and 30% larger than that of bcc Fe, respectively. Fe is immiscible with Cd in the entire composition range of the equilibrium phase diagram,[4] while Fe in Zn is nonalloying for iron concentrations of less than 5 at. %.[4] Both Cd and Zn crystallize in a hexagonal structure, with a high c/a ratio.

The films were prepared in a liquid He cryostat by thermal co-evaporation of high purity iron (98% enriched in [57]Fe), Cd, and Zn (99.999%) metals from two independent resistively heated Ta ovens. The deposition was performed onto kapton substrates tilted 45° relative to the vapor metal flux direction and the gamma ray direction, the substrate temperature were 16 K and 300 K, with a base pressure of 3×10^{-9} mbar and residual pressure of 2×10^{-8} mbar during the evaporation. The deposition rates were controlled using quartz crystals of 5 MHz frequency and a home-made deposimeter. We used deposition rates of 0.01 Å/s and 2.0 Å/s for the Fe and the matrix, respectively. All films have a nominal thickness of 4000 Å. Our experimental setup[11] is especially suitable for the present study because it allows *in situ* measurements of MS under external magnetic field and resistivity. The MS measurements were performed using a 25 mCi [57]Co:*Rh* source moving in a sinusoidal mode; source and absorber were kept at the same temperature. The IS values reported are relative to bcc iron at room temperature.

Resistivity measurements were performed *in situ* by a conventional four-electrode method. Four points of silver (99.99% of purity) as electrical contacts were deposited onto the kapton substrate before depositing the Cd and Fe metals.

III. THEORETICAL APPROACH

Here, we use the real-space linear-muffin-tin orbital method, within the atomic sphere approximation (RS-LMTO-ASA), to obtain the IS of a substitutional Fe impurity in hcp Cd and Zn. This is a first-principles, self-consistent RS-LMTO-ASA approach[12] which follows the steps of the LMTO-ASA formalism,[13] but uses the recursion method[14] to solve the eigenvalue problem directly in real space. It is a linear method and the solutions are accurate near a given energy E_ν, here taken at the center of gravity of the band. We work in the orthogonal representation and expand the Hamiltonian in terms of tight-binding parameters, neglecting terms of order $(E - E_\nu)^3$ and higher. The Hamiltonian can then be written as[13]

$$H = E_\nu + h - \bar{h}\bar{o}\bar{h}, \qquad (1)$$

where $\bar{o}$ is a potential parameter and $\bar{h}$ is a Hermitian matrix, which can be written in terms of the structure constant and the potential parameters of the tight-binding LMTO-ASA representation. To solve the eigenvalue problem in real space, we consider a large cluster to simulate the system, and use the recursion method with the Beer-Pettifor terminator[15]

to complete the recursion chain. The calculations were performed using clusters of 6000 host (Cd or Zn) atoms arranged in the appropriate hcp structure, with one of the central atoms substituted by Fe. We have considered a basis of s, p, and d electrons (9 orbital per site) and have used 20 levels of recursion. We work within the local spin density approximation with the exchange and correlation potential of von Barth and Hedin.[16]

The theoretical approach is essentially the one used by Terrazos and Frota-Pessôa,[9] but while here we include terms in $(E - E_\nu)^2$; in the previous work these second-order terms [related to $\bar{h}\bar{o}\bar{h}$ in the Hamiltonian of Eq. (1)] were neglected. It is clear from Fig. 1 that the first-order approximation describes rather well the IS trends, but since both Cd and Zn have wide s bands, the inclusion of second-order terms may be relevant. As in the previous work, the IS at the Fe site is obtained in terms of the calculated electronic charge density $\rho^{imp}(r)$ at the Fe impurity and $\rho^{Fe}(r)$ at the Fe site in bcc Fe (taken as reference), both substituted at the nuclear region by taking $r = 0$. In units of mm/s, taking the usual factor α to be used in nonrelativistic calculations, we have

$$\mathrm{IS} = \alpha[\rho^{imp}(0) - \rho^{Fe}(0)]. \qquad (2)$$

The constant $\alpha = -0.24$ is given in units of a_0^3 mm/s. A more detailed description of the IS calculations, as well as a simple model to interpret the results, can be found elsewhere.[9]

The magnetic properties of Fe in Al, Cd, and Zn are interesting and have been investigated experimentally and theoretically by several groups. Theoretically the moment of Fe in Al vanishes when lattice relaxation is taken into account,[17] while the Fe impurities in Cd and Zn seem to retain their moments in the presence of relaxation.[18] Magnetic studies using Fe implantation and the TDPAD technique reported for the Fe:Cd system by Funk[19] suggest that Fe impurities in Cd could be magnetic, with high Kondo temperatures over 370 K. But to our knowledge, in spite of the theoretical predictions, no evidence of magnetism for Fe in Zn has been detected so far. Here we do not address the magnetic properties, which will be discussed in a following paper. But considering that the existence of moments is controversial in these systems, the IS of Fe was obtained considering both spin-polarized and nonmagnetic Fe impurities in Cd and Zn.

IV. RESULTS AND DISCUSSION

Here we present our experimental results for Fe:*Zn* (Sec. IV A) and Fe:*Cd* (Sec. IV B). In the case of Fe in Zn the Mössbauer spectra suggest that the Fe impurity occupies one type of site, while for Fe in Cd the MS results indicate that more than one type of site can be occupied by Fe. In Sec. IV C we consider the Fe impurities in both Zn and Cd and, with the help of theoretical calculations, establish values for the IS of substitutional Fe sites in these systems. These values are discussed and compared with those in the literature.
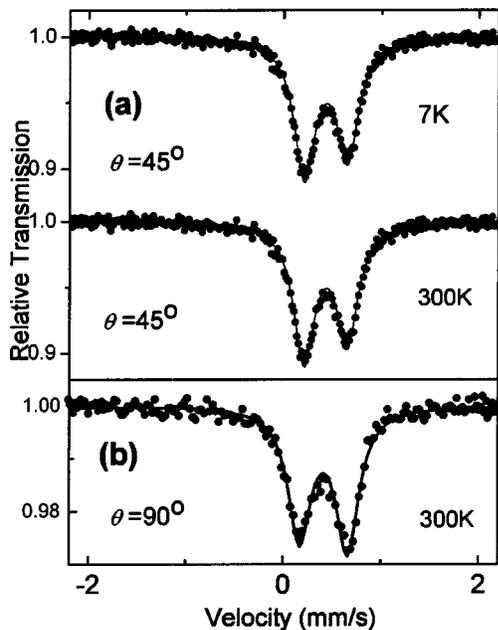
FIG. 2. (a) MS measured at 7 K and 300 K for the film $Fe_{0.005}Zn_{0.995}$, prepared at 300 K, the measurements were performed as indicated in Sec. II, (b) MS measured at 300 K and at 90° between the film plane and the γ-ray direction.

A. Fe:*Zn*

We have prepared several samples of Fe in a Zn matrix, using vapor quenching at low temperatures; however, the best sample, as revealed by Mössbauer spectroscopy, was obtained with the substrate at 300 K. Figure 2(a) shows the *in situ* MS for this sample at two different temperatures, 7 K and 300 K. The spectrum shows a narrow slightly asymmetric paramagnetic doublet, which has been associated with a component corresponding to a single-type Fe location. The asymmetry of the spectra was attributed to the presence of texture effects. This is confirmed by additional MS measurements showing the expected angular dependence of that asymmetry [see Fig. 2(b)]. The hyperfine parameters are IS $=0.53(1)$ mm/s and the quadrupole splitting is 0.5 mm/s; the linewidth in all ranges of temperatures considered was 0.28 mm/s, indicating that the sample is stable and confirming that the Fe impurities are present in a unique phase. The values of isomer shift, within the measurement error, and quadrupole splitting (QS) are in good agreement with the values of IS $=0.51$ mm/s and QS$=0.5$ (Refs. 1 and 10) reported in the literature for Fe in Zn.

B. Fe:*Cd*

The *in situ* Mössbauer spectrum at 7 K, for the as-prepared ^{57}Fe:*Cd* film, is displayed as the top spectrum in Fig. 3. It consists of a main doublet (doublet I) with isomer shift IS(I)$=0.74(1)$ mm/s, quadrupole splitting QS(I) $=0.61(1)$ mm/s, and 91% relative absorption area (RAA). The large positive IS value found for the doublet (I) is expected for substitutional Fe sites in hosts with large Wigner-Seitz (WS) radius, since in the case of large atomic volumes, the *s*-electron density at the nuclear site is small ($\Delta R/R$
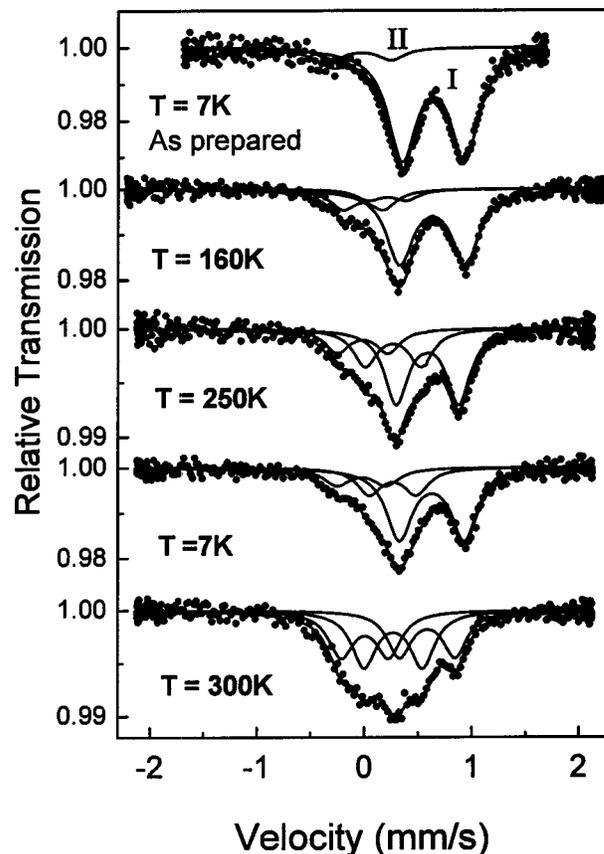

FIG. 3. *In situ* MS at different temperatures for the $Fe_{0.005}Cd_{0.995}$ film prepared at 16 K.

<0, for ^{57}Fe). Near zero velocity, a small doublet (II) is observed with IS(II)$=0.08(1)$ mm/s and QS(II) $=0.55(2)$ mm/s. This subspectrum reflects a higher electron density at the nuclear site and could be due either to Fe in interstitial sites or to small iron clusters.

In order to investigate possible cluster formation due to atomic diffusion in the films, we have performed *in situ* Mössbauer measurements at higher temperatures. The corresponding MS can also be seen in Fig. 3. In the first annealing, as the temperature is increased to 250 K, a new Fe component appears (doublet III) with IS(III)$=0.30$ mm/s and QS(III)$=0.50$ mm/s. Changes in the relative absorption area during annealing, as well as values for the IS and the QS, are given in Table I. One can see that as the temperature rises from 7 K to 250 K, the RAA of doublets II and III steadily increases while the RAA of doublet I decreases. If the heated sample is again cooled down to 7 K the process is not completely reversed: part of the new phase (doublet III) remains and retains a significant RAA of 22%. We note that in the cooled sample, the RAA of doublet II increases from 9% to 15%, while that of doublet I decreases from 91% to 63%, when compared to the as-prepared system. The differences in the RAA observed at 250 K and 7 K indicate that doublet I has a lower Debye temperature than doublets II and III. As the temperature is again increased to 300 K, we observe an increase in the relative areas of doublets II and III at the expense of the main doublet I. The behavior described

TABLE I. Hyperfine parameters of the $Fe_{0.005}Cd_{0.995}$ film, $T_s = 16$ K. IS and QS are in mm/s; RAA is in %.

T(K)	Doublet I			Doublet II			Doublet III		
	IS	QS	RAA	IS	QS	RAA	IS	QS	RAA
7	0.74(1)	0.61(1)	91	0.08(1)	0.55(2)	9			
160	0.72(1)	0.62(1)	73	0.08(1)	0.51(2)	12	0.33(2)	0.5(5)	15
250	0.70(1)	0.58(1)	54	0.09(1)	0.47(2)	18	0.35(1)	0.54(2)	28
7	0.70(1)	0.60(1)	63	0.10(1)	0.45(2)	15	0.37(1)	0.52(2)	22
300	0.70(1)	0.52(1)	31	0.08(1)	0.44(2)	31	0.37(1)	0.51(2)	38

above for this low-solubility system is different from that observed in Fe:*Pb* and Fe:*Yb*.[6] In these systems, after annealing at 300 K, all isolated Fe atoms diffuse, forming small clusters, and the signal corresponding to the isolated impurities disappears. Here a fraction of the main doublet remains, but analogy suggests that the new phase III could be related to the formation of small iron clusters such as dimers, trimers, etc.

After annealing the sample up to 250 K the isomer shift value of the doublet I decreases by 0.04 mm/s and remains at 0.7 mm/s up to 300 K and the quadruple splitting decreases by 0.02 mm/s, which could be due to annealing of defects present in the quench-condensed film. Thus, after annealing the sample has a rather crystalline structure.

It is well known that the vapor condensation of nonmiscible metals at high temperatures favors metal clustering. Thus, to investigate if the appearance of doublet III and the increase in RAA of doublet II could be correlated to the formation of Fe clusters during annealing, we have prepared a sample with a 0.5 at. % of ^{57}Fe at 300 K, using deposition rates and vacuum conditions similar to those of the sample prepared at 7 K. The MS, taken at different temperatures between 11 K and 300 K, is shown in Fig. 4. Analysis of these data shows that the MS consists of two doublets with hyperfine parameters similar to those observed before, which we denote as doublets II and III. In Fig. 5 we show the relative RAA variation for doublets II and III in the Fe:*Cd* samples prepared at 300 K. The RAA of the site corresponding to doublet II, when measured at low temperatures, is higher than that of the site identified with doublet III, indicating that it has a lower Debye temperature. The same behavior was observed for doublets II and III in the sample prepared at 16 K, reinforcing the assumption that these doublets are really associated with small Fe clusters in Cd.

In Fig. 6 we show the results of *in situ* ac resistivity measurements performed on a Cd film with iron concentration of 0.5 at. %, prepared at 16 K. Initially, as we heat the sample, the electrical resistivity increases, i.e., it has a positive temperature coefficient up to about 120 K. However, above this temperature the temperature coefficient of the resistivity is becoming negative, indicating that defects are being annealed. Cooling the sample back from 220 K to low temperatures, the resistivity curve shows that the annealed sample has a resistivity which is a factor of about 2 smaller than that of the as-prepared sample. This relative small

change in the resistivity and the small variation of the hyperfine parameters observed in the MS measurements of the annealed sample confirm our interpretation that the as-prepared Fe-Cd film has a rather crystalline structure containing some defects. Increasing the temperature again to 300 K, the resistivity curve was reproduced, showing the completely reversible behavior of the annealed sample typical for a rather crystalline sample. In the range of temperatures accessed in our experiment no indication of Kondo-like behavior was observed.

C. Substitutional Fe impurities in Cd and Zn

As shown in Fig. 1, first-principles LDA calculations for the IS of substitutional Fe impurities in a large number of
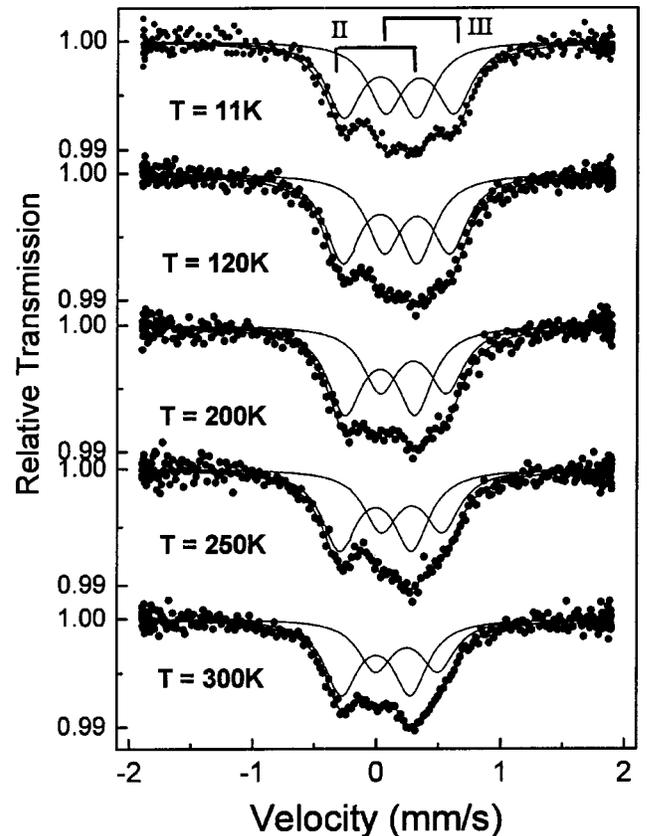

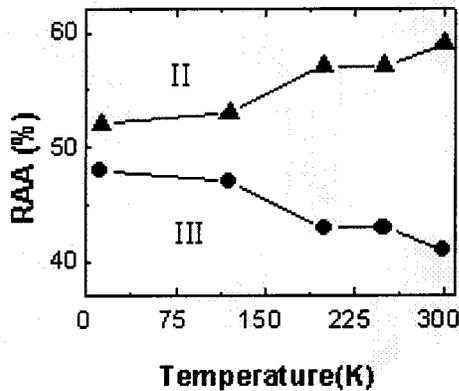FIG. 4. MS measured at different temperatures for the film $Fe_{0.005}Cd_{0.995}$ prepared at 300 K.

FIG. 5. Relative absorption area (RAA) vs temperature variations for the $Fe_{0.005}Cd_{0.995}$ film prepared at 300 K.

TABLE II. Theoretical and experimental IS for substitutional Fe in Cd and Zn hosts, SP and NP mean spin polarized and nonpolarized, respectively.

Host	SP (mm/s)	NP (mm/s)	Expt. (mm/s)
Zn	0.47	0.53	0.53(1)
Cd	0.57	0.66	0.70(1)

In Table II are shown the theoretical results for the IS of substitutional Fe impurities in Zn and Cd. The results were calculated using the procedure described in Sec. III and, for the reasons discussed there, both the spin polarized (SP) and nonpolarized (NP) situations considered. As noted previously,[9] IS results for the spin-polarized case are usually lower than the ones obtained for the nonmagnetic impurity and this can be seen for Fe in Zn and Cd. We also know from previous calculations[9] that the core contributions should be small. Here, in all cases, core contributions are responsible for less than 10% of the IS value.

In Table II, together with the theoretical results, the experimental IS values for Fe in Cd and Zn are also shown for comparison. In the case of Cd, where several components are present, the value corresponding to doublet I was assumed to represent substitutional Fe impurities in Cd, since, as we discussed in Sec. IV B, the other doublets are probably associated with small Fe clusters. Since resistivity measurements suggest that the Cd film, deposited at 16 K, as prepared, might be with some disorder, we have taken the of IS $=0.70$ mm/s associated with the rather crystalline films in Table I to represent the experimental value for Fe impurities in Cd. Considering that in first-principles calculations no adjustable parameters are used, the agreement between theory and experiment in Table II is rather good, suggesting that the IS of Fe in Cd is really much larger than previously reported and confirming our assignment of doublet I as corresponding to substitutional Fe impurities in Cd.

Finally, in Fig. 7, we show trends in the IS for substitutional Fe impurities in several hosts to the right of Fe in the periodic table. Theoretical results of Terrazos and Frota-Pessôa (black squares) and experimental results found in the literature (empty circles) are shown together with the new IS theoretical (open square) and experimental IS results for Fe in Cd and Zn obtained from MS in this paper (cross). We note that our experimental value of 0.53(1) mm/s for the IS of Fe in Zn is in good agreement with those of 0.51(1) mm/s and 0.53(1) mm/s found in the literature, but for Fe in Cd our present value of 0.70(1) mm/s is substantially higher than the one (0.45 mm/s) previously reported. This lower old value actually is closer to that of doublet II and may be associated with clustering or other defects in the sample. If our result (cross) is considered, the experimental result for the IS of Fe in Cd is slightly higher than the theoretical one, and fits perfectly into the trends established by the behavior in other hosts. These trends can be understood in terms of a simple model where the IS of Fe is mainly governed by the WS radius of the host that gives the volume available for the Fe when introduced substitutionally into a given host. Interstitial Fe impurities tend to have more negative IS values since

metallic hosts give results which reproduce well the observed experimental tendencies. These results,[9] which can be understood in terms of a simple model, were obtained using the RS-LMTO-ASA approach in the first-order approximation, in which the term $\bar{h}\bar{o}\bar{h}$ of Eq. (1) is neglected. As mentioned before, we observe that for simple metal hosts to the right of Fe [Fig. 1(b)], the calculated IS values (black squares) are systematically lower than the experimental values reported in the literature (empty circles). The noticeable exception is Cd, suggesting that the reported experimental IS value for Fe in this host may be too low.

Here, we present new measurements for the IS of Fe in two hosts: Zn (which, in the comparison of Fig. 1 followed the expected trends) and Cd (which apparently did not). Since the second-order term $\bar{h}\bar{o}\bar{h}$ may be of some importance in the case of hosts with broad s bands, the IS calculations for substitutional Fe in Zn and Cd were repeated, taking these terms into account. As in the measurements, the IS values were obtained using bcc Fe as the reference system.
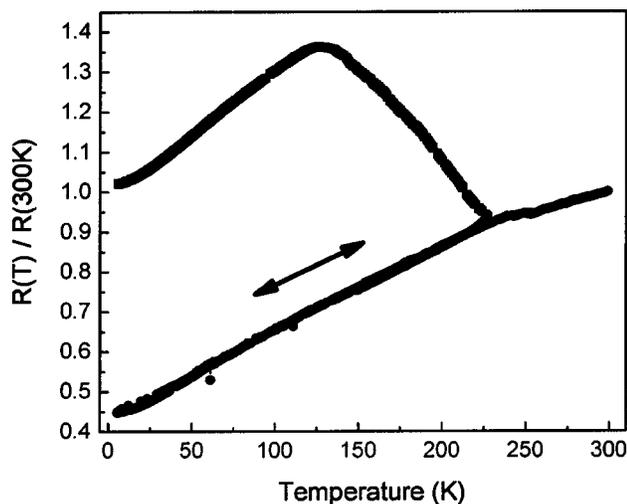

FIG. 6. Electrical resistivity as a function of temperature of as-prepared Fe:Cd film. Reversible branches of the curves are marked with double arrows.
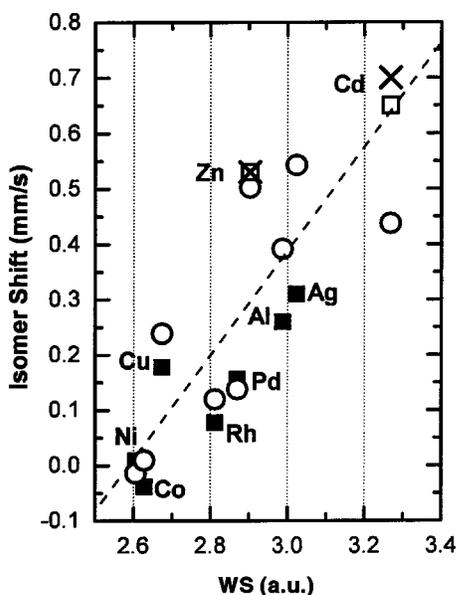
FIG. 7. Isomer shift values for substitutional Fe impurities in several hosts to the right of Fe in the periodic table. Some experimental (empty circles) and theoretical (black squares) results as in Ref. 9 are given together with the new experimental IS values for Fe in Zn and Cd (cross) and theoretical IS values (empty squares), obtained here.

compression increases the electronic charge density at the nucleus.[8] Similarly, as the volume occupied by the substitutional Fe impurity in the host increases, the IS at the impurity increases, reflecting a lower *s*-electron charge density at the Fe nucleus. Since the WS radius of Cd (3.24 a.u.) is larger than that of Zn (2.98 a.u.), the IS for Fe in Zn should be smaller than that of Fe in Cd and this is in fact observed in the present results.

V. CONCLUSIONS

Here we have used the vapor condensation method to produce Zn and Cd films with low concentrations of ^{57}Fe and have shown that reliable, stable samples of these nonalloying systems can be obtained using this technique. The films were

then studied, at several temperatures, using *in situ* Mössbauer spectroscopy and *in situ* resistivity measurements. In the case of Fe in Zn, we found that the Fe occupies only one site, with IS=0.53(1) mm/s and a QS=0.5(1) mm/s, even for deposition with the substrate at room temperature. This behavior is different from what we have found for Fe in Pb and in Yb films,[7] and it would be important to understand this difference. For Fe in Cd, the situation is more complex, and at higher temperatures the MS indicate coexistence of three different Fe sites. To identify the sites we have prepared the Cd films not only at 16 K, but also at a much higher temperature (300 K), where formation of Fe clusters is favored. Doublet I, which dominates at low temperatures with an IS of around 0.70(1) mm/s and a QS =0.60(1) mm/s, has been associated with substitutional Fe impurities, while the other two doublets are associated with the formation of small Fe clusters.

We have also performed first-principles calculations for the IS of substitutional Fe impurities in Zn and Cd. The identification of doublet I with substitutional Fe impurities is supported by these calculations.

We used experimental and theoretical approaches to investigate the behavior of the isomer shift of Fe impurities in Cd and Zn. The experimental IS values agree well with those obtained in the calculations and follow the expected trends as a function of the volume available for the Fe,[9] which, in the case of substitutional impurities, is determined by the Wigner-Seitz radius of the host. Our experimental value of 0.53(1) mm/s for the IS of Fe in Zn is in good agreement with those reported in the literature.[1,10] A new, more reliable IS value of 0.70 (1)mm/s has been determined for substitutional Fe impurities in Cd, confirming that the previous value of 0.45 mm/s (Ref. 1) was too low.

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