

The Ferromagnetic and half metallic behaviors of Fe- and Co- doped SnO₂ within Local Density Approximation and Self-Interaction-Corrected

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Abstract

Using ab-initio calculation based on the Korringa-Kohn-Rostoker Coherent Potential Approximation (KKR-CPA) method in connection with the local density approximation without and within self-interaction-corrected (LDA and LDA-SIC), we represent a theoretical study of the SnO₂ doped system with transition metals (TM) which are Iron (Fe) and Cobalt (Co). In this system, the stability of the ferromagnetic state compared with the spin-glass state is investigated by comparing their total energies. The Ferromagnetic and half metallic behaviors was observed and conformed with the local-moment-disordered (LMD) state energy for LDA (local density approximation) and LDA-SIC (local density approximation-self-interaction correction) approximation in [Sn_{0.95}TM_{0.05}(Fe or Co)]O₂. Based on mean field method, the Curie temperature is estimated. To explain the origin of magnetic behavior, we give information about total and atom projected density of states functions of Fe and Co elements and we propose a model which describes magnetic interaction in [Sn_{0.95}TM_{0.05}(Fe or Co)]O₂.

Keywords: Self-interaction-corrected, Diluted magnetic semiconductors, Ferromagnetic, Magnetic properties, Curie temperature, SnO₂.

I. Introduction

In recent years, dilute magnetic semiconductors (DMS) systems have drawn enormous interest in the scientific community [1]. This is due to their potential for application in spintronic devices. Tin dioxide (SnO₂) has been used for development of different applications [2]. In particular, according to its excellent optical and electrical properties, as well as outstanding chemical and physical stabilities, SnO₂ has been extensively explored in photovoltaic device technology [3] and flat-panel displays in the field of transparent conducting electrodes [4]. It is recalled, SnO₂ is an n-type semiconductor with direct wide band gap $E_g=3.6$ eV [5]. This propriety has received deeper interest for a new generation of spintronics [6], in which

one seeks the ferromagnetic semiconductors at Curie temperatures well above room temperature.

For these reasons, many efforts have been devoted to the theoretical and experimental studies of the magnetic properties of SnO₂ doped with various transition metals, such as Fe, Co, Mn, Cr, V, Ni, Mn/W and Zn/Mn [7-18]. However, few theoretical studies on SnO₂ doped with some transition metals, have been done using the Self-Interaction-Corrected (SIC) developed by Perdew and Zunger [19] in order to investigate the magnetic properties. This latter, may change the stability of ferromagnetic states to spin glass states by co-doping or by native point defect in the structure [20]. Hongxia Wang et al. used another type of correction GGA- U approximation before and after introducing the oxygen vacancies (V_O) in SnO₂ doped with 5% of Cobalt. They show that the most stable magnetic

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state is the antiferromagnetic and ferromagnetic before and after creating V_O , respectively [21].

In this work, our calculations based on the Korringa-Kohn-Rostoker Coherent Potential Approximation (KKR-CPA) method employing the local density approximation without and within self-interaction-corrected (LDA and LDA-SIC) code [22, 23], have been done in order to study the effect of localization and delocalization of 3d shell of Fe and Co doped SnO_2 , on electronic structure and magnetic properties variations. In one hand, the stability of magnetic states in $(\text{Sn}, \text{TM}=\text{Fe or Co})\text{O}_2$ doped system with LDA and LDA-SIC approximation is discussed. The ferromagnetic state (FM) and the disordered local moment (DLM) state are considered. Based on the Heisenberg model within mean field approximation, the Curie temperature (T_C) is estimated from the total energy difference between the (DLM) and the (FM) state. The values corresponding to T_C in our system is in good agreement with the experimental observations [11, 12]. Moreover, when we used SIC correction, the Curie temperature increases in SnO_2 doped with Fe. In other hand, to explain the stability of ferromagnetism states variation in our system between LDA and LDA-SIC, the density of state and band structure have been calculated.

This paper is organized as follows: The Crystal structure and calculation method are briefly described in section 2, the results and discussions are presented in section 3, and a conclusions is given in section 4.

II. Calculation method and crystal structure

Here, our present calculations based on the density functional theory using the Korringa Kohn Rostoker III. method combined with the coherent potential approximation within the local spin density approximation IV. (KKR-CPA-LSDA) which enables us to take into account the randomness of the impurity elements. In our numerical simulations, we use the KKR-CPA-SIC-LSDA package, in which SIC developed by Toyoda et al. [23], and it is implemented into MACHIKANEYAMA2002 [24]. The local spin density approximation (LSDA) is based on the parameterization given by Moruzzi, Janak and Williams (MJW) [25]. The relativistic effect has been considered using the scalar relativistic approximation. Moreover, the potential form is approximately given by the muffin tin model. The corresponding wave functions in the muffin-tin spheres have been expanded with the real harmonics up to $l=2$, where l is the angular momentum defined at different

sites. In what follows, we use higher K-points up to 500 in the irreducible part of the first Brillouin Zone.

Our Calculations will be based on the rutile structure of SnO_2 . This crystalline structure has tetragonal unit cell with two lattice parameters ("a" and "c") and an extra internal parameter u defined as the length of the bond parallel to the c axis, in units of c . Here we specify the lattice parameter of SnO_2 and lattice parameter $a = b = 4.7373 \text{ \AA}$, $c = 3.1864 \text{ \AA}$ and $u = 0.307$ [26].

It is worth noting that for each atom the sphere radius is taken such that the volume of the unit cell is the sum of the volumes of the all atomic spheres. In order to achieve a good packing [27], we should add initially "empty" spheres (ES) with ($Z = 0$) representing atomic inter-sites. Using the space group $P4_2/mnm$ in the International Tables of X-ray Crystallography Table N°136, we put the six atoms, two tin atoms occupying 2a Wyckoff positions: $(0,0,0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and four oxygen ions occupying 4f positions: $(u,u,0)$ $(-u,-u,0)$ $(\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})$ $(\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2})$, while a set of eight ES has been localized at the positions : $(\frac{1}{2}, 0, 0.1682)$ $(0, \frac{1}{2}, -0.1682)$ $(0, \frac{1}{2}, 0.1682)$ $(\frac{1}{2}, 0, 0.1682)$ $(-0.3125, 0.3125, 0)$ $(-0.1875, -0.1875, 0)$ $(0.1875, 0.1875, 0)$, $(0.3125, -0.3125, 0)$. This atomic configuration is presented in Fig.1.

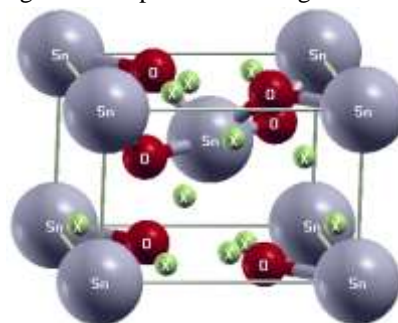


Fig.1: The unit cell of SnO_2

The atoms were considered as the valence states for Sn ($4d^{10}5s^25p^2$), Fe ($3d^64s^2$), Co ($3d^74s^2$) and O ($2s^22p^4$).

III. Results and discussions

In this part, based on the method mentioned above, we study the electronic structure of SnO_2 having the rutile structure. Fig.2 reveals the total density of states (DOS) of SnO_2 as well as partial DOS related to Sn ($5p$) and O ($2p$). It follows that there are two parts in the valence band (VB). In the first part, the band with energy range from -0.55 to -0.18 Ry is called high VB, and the second part concerns the band with energy range from -0.7 to -0.55 Ry which is called short VB. For both part, we found strong $5p$ character of Sn states. While the contribution of the lowest conduction band (CB) are fully from -0.015 Ry of O ($2p$) states. The density of states (DOS) of majority and minority

spin are symmetrical. Therefore, there is no evidence of magnetic property. From the DOS of SnO_2 (Fig.2), the value of band gap calculated is 2.1 eV, which is smaller than the experimental value (3.6 eV) [5]. This difference is a perfect argument with LDA approximation, which is known to underestimate the band gap [28].

In order to verify the type of band gap and their value in SnO_2 , we have been drawn their band structure in Fig.3.

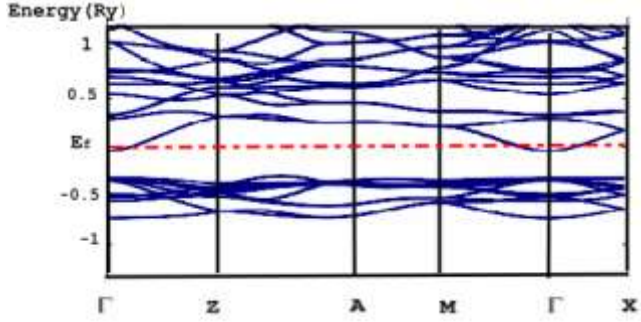


Fig. 3: The band structure of bulk SnO_2

This latter show the SnO_2 having a direct band gap ($E_{\Gamma-\Gamma}$), which is corresponding the lowest energy electron-hole transition occurring at the Γ point. The value of gap between this transitions is similar of that obtained by DOS. The band structure of SnO_2 has three bands of energy. Based on density of states, the first band, having the low energy range from -1.2 to -1.5 Ry, is essentially composed by the semi-core of Sn (4d) states, the second band corresponding of valence band concerning of energy interval between -0.7 and -0.2 Ry, in which we have the hybridized between O (2p) and Sn (5p) states, and the last is corresponding the conduction band which is higher on the energy scale is built of the 5s states of tin, which are typical for SnO_2 as well as with the results of previous calculations [29, 30].

1. Magnetic properties in Fe and Co doped SnO_2

In this part, we study the magnetic properties of SnO_2 , doped in Sn positions with 5% of single transition elements TM, which are Iron (Fe) and Cobalt (Co), in order to compare with experimental observations [11, 12]. Doping with 5% of TM (Fe or Co) ion can be changed the magnetic propriety of SnO_2 . The result of magnetism in $[\text{Sn}_{0.95}\text{TM}_{0.05}(\text{Fe or Co})]\text{O}_2$ is illustrate in Table 1, which shows that the Fe and Co doped SnO_2 have magnetic moments are $3.95\mu_B$ and $3.54\mu_B$ respectively with LDA, but when we add the SIC approximation the magnetic moments are $4.34\mu_B$ and $3.39\mu_B$.

In order to determine the most stable magnetic state, the energy difference

$$\Delta E = E(\text{Spin-glass State}) - E(\text{Ferromagnetic State}) \quad (1)$$

(as shown in Ref. [31]) between the ferromagnetic state (FM) and the disordered local moment (DLM) has been calculated. DLM state describes the spin-glass state at finite temperature [32] where the directions of all local moments are randomly distributed, so that the average magnetization vanishes.

Approximations	Fe- doped SnO_2		Co- doped SnO_2	
	LDA	LDA-SIC	LDA	LDA-SIC
$M^T (\mu_B)$	0.2174	0.2277	-0.1995	0.1843
$M^{\text{TM}} (\mu_B)$	3.95	4.34	-3.54	3.39
$M^O (\mu_B)$	0.00485	0.00095	-0.00941	0.00293
$\Delta E (\text{meV})$	3.98	5.02	5.26	5.08
$T_C (\text{K})$	615.29	776.06	813.94	812.55

Table 1: Total magnetic moments of the unit cell (M^T), magnetic moments of Fe and Co atoms (M^{TM}), its nearest neighbor O atoms (M^O), the energies difference (ΔE) and the Curie temperature (T_C).

The variation of the ΔE as function of the TM (Fe, Co) and the type of approximations (LDA and LDA-SIC) are given in Table 1, in which is shown that ΔE has always positive values. These indicate that the ferromagnetic state is more stable than the spin glass for both cases, and it is correlated with experimental results [11, 12] and with theoretical results [33, 34].

However, using another correction U_{Co} coupled with GGA approximation, Hongxia Wang et al. have been found the anti-ferromagnetic state is most stable in SnO_2 doped with 5% of Co without the oxygen vacancies (V_O), and the ferromagnetic state becomes more stable than anti-ferromagnetic state when they introduce the V_O [21]. There is contradiction between this result and our contribution. This difference observed can be explained by the fact that the introduction of SIC can make the correction automatically, unlike of U_{Co} .

Based on mean field method (MFA), the Curie temperature (T_C) can be estimated from the total energy difference between the DLM and the ferromagnetic state by the following equation:

$$k_B T_C = \frac{2}{3} \frac{\Delta E}{c} \quad (2)$$

Where c is the concentration of magnetic impurities. For $\text{Sn}_{0.95}\text{TM}_{0.05}(\text{Fe or Co})\text{O}_2$ doped system, the results of T_C calculations are summarized in Table 1, in which is shown that the Curie temperatures have a high value for our system. The results of LDA approximation are a good agreement with the experimental observations found by J. M. D. Coey et al. and S. B. Ogale et al. [11, 12] in SnO_2 films doped Fe or Co synthesis by pulsed-laser deposition method, in which the values of Curie temperature obtained are 610 K and 650 K respectively for Fe and Co. However,

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for LDA-SIC approximation, T_C is higher than obtained value by LDA in SnO₂ doped with Fe, and T_C is similar as found by LDA in SnO₂ doped with Co.

2. Electronic structure in Fe and Co doped SnO₂

In order to understand and to explain the more stabilized ferromagnetism state in Sn_{0.95}TM_{0.05}(Fe or Co)O₂ doped system, the density of states (DOS) of this system for LDA without and within SIC was calculated. Fig.4 (a,b) and 5 (a,b) represents the DOS respectively of SnO₂ doped Co and Fe.

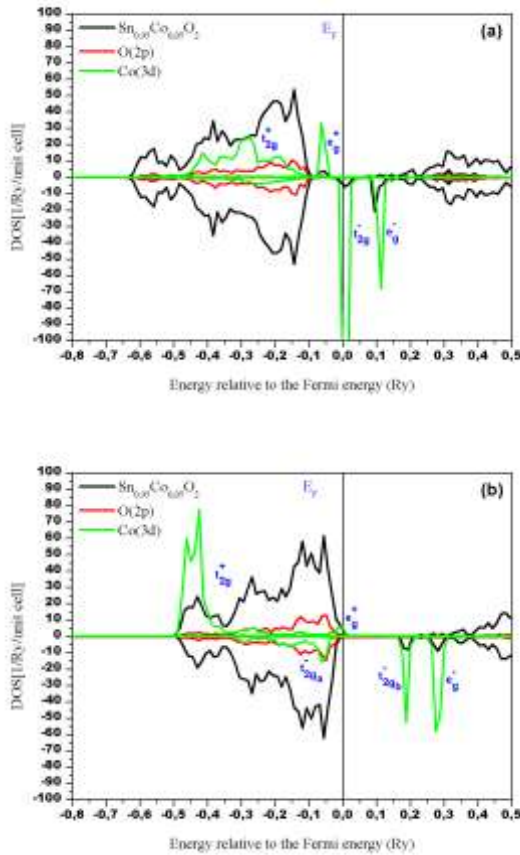


Fig. 4: The PDOS of Co (3d) and O (2p) (green, red) and TDOS (black) of Co- doped SnO₂ in the case of 5% doping are shown in (a, b), with LDA without and within SIC respectively.

Known that the Co (3d⁷ 4s²) and Fe (3d⁶ 4s²) have respectively nine and eight electrons and in SnO₂ system which are doped in octahedral site of Sn, it become Co⁴⁺ (3d⁵) and Fe⁴⁺ (3d⁴) with five and four electrons respectively. Also, the d orbital is divided into two states t_{2g} (d_{xy} , d_{yz} , d_{zx}) and e_g ($d_{x^2-y^2}$, d_{z^2}) with respectively low and high energy due to electrostatic field created by six ligand (octahedral crystal field) see in Fig.4 and 5. For LDA approximation of 5% of Co doping in SnO₂, the five electrons in 3d are occupied with 3 spins up in t_{2g} state and

2 spin up in e_g state. The exchange splitting between t_{2g} states is larger than the crystal field splitting between t_{2g} and e_g states in this case. Besides from Fig.4 (b), when we add SIC approximation to LDA, we observed the modification of arrangement in electronic structure, such that we obtain 4 electrons in t_{2g} state instead of 3 electrons, with 3 is on spin up, and 1 on spin down, and the remaining 1 is on spin up in e_g state, which leads to Jahn teller effect. Indeed, after the rule of Jahn teller effect that t_{2g} states for down and up-spin side are leading to a formation of t_{2g} fractions, is indicate in Fig.6. This effect is responsible to find nearly a some partial moments of Cobalt.

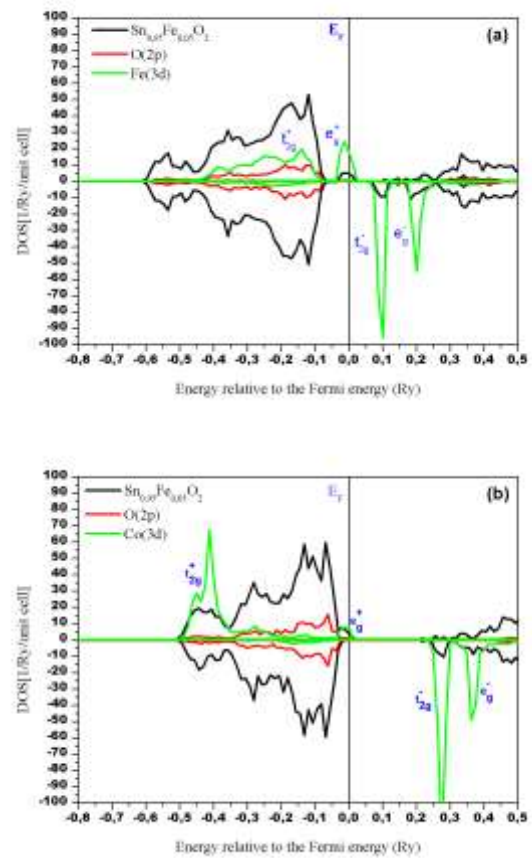


Fig. 5: The PDOS of Fe (3d) and O (2p) (green, red) and TDOS (black) of Fe- doped SnO₂ in the case of 5% doping are shown in (a) (b), with LDA without and within SIC respectively.

Fig.5 (a) and (b) shows the calculated DOS of (Sn_{0.95}, Fe_{0.05})O₂ DMS within standard LDA and LDA-SIC, respectively. Generally speaking, considering the formal electron configurations, d⁴ electron configurations are realized for Fe⁴⁺. In case of LDA (Fig.5 (a)), Fermi energy appears inside e_g states for up-spin side to t_{2g} states and half-metallic density of states is also predicted, so that the formal electron configuration leads to magnetic moments of 3.95 μ_B per Fe atom. In case of LDA-SIC (Fig.5 (b)), on one

hand, t_{2g} states for up-spin side are splitting, leading to a formation of t_{2g} fractions that is present in Fig. 6. The Fermi energy appears inside both of e_g states for up-spin side and the t_{2g} fraction for down-spin side. As a result a calculated magnetic moment value per Fe atom is $4.34 \mu_B$. This augmentation in partial moments leads to increase of the Curie temperature of 615.29 to 776.06 K.

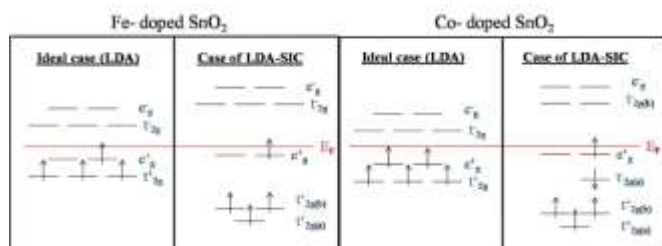


Fig.6: Jahn teller effect in Fe and Co doped SnO_2 with LDA without and within SIC

On the other hand, the peak of the partial density of Fe-d states (t_{2g} states for up-spin side) is agree with a photoemission (XPS) spectra result reported by C. Ke et al. [35].

IV. Conclusion

In conclusion, the peculiarities of the band gap between the density of states and the band structure in pure SnO_2 is comparable. The electronic structures and the magnetic properties for $\text{Sn}_{1-x}\text{TM}_x\text{O}_2$, $x=0.05$ and $\text{TM}=\text{Fe}$ and Co , were investigated using the KKR-CPA method in connection with the LDA without and within SIC. Our calculations show that the ferromagnetic state is more stable than the spin glass for both cases, and it is correlated with experimental and theoretical results. After the introduction of the Self-Interaction-Corrected (SIC) to LDA we obtained the localization of t_{2g} band of every TM-doped SnO_2 and appearance of Jahn Teller effect. This localization leads to increase of the Curie temperature in Fe-doped SnO_2 of 615.29 to 776.06 K.

References

- [1] S. Chattopadhyay, S. K. Neogi, A. Sarkar, M. D. Mukadam, S. M. Yusuf, A. Banerjee and S. Bandyopadhyay, J. Magn. Magn. Mater. 323 (2011) 363-368.
- [2] M. Batzill and U. Diebold, Prog. Surf. Sci. 79 (2005) 47-154.
- [3] H. L. Hartnagel, A. L. Dewar, A. K. Jain and C. Jagadish, Semiconducting Transparent Thin Films, IOP, Bristol, 1955.
- [4] B. G. Lewis and D. C. Paine, MRS Bull. 25 (2000) 22-27.
- [5] R. Wyckoff, Crystal Structures, 2nd ed., Vol. 1 (Interscience, New York, 1964).
- [6] Spin Electronics, M. Ziese and M.J. Thornton (Eds.), Lecture Notes in Physics Vol. 569, Springer, Berlin (2001).
- [7] N. H. Hong and J. Sakai, Physica B: Condens. Matter 358 (2005) 265-268.
- [8] N. H. Hong, J. Sakai, W. Prellier and A. Hassini, J. Phys.: Condens. Matter 17 (2005) 1697-1702.
- [9] Y. Lu, P.-J. Wang, C.-W. Zhang, X.-Y. Feng, L. Jiang and G.-L. Zhang, Physica B: Condens. Matter 406 (2011) 31373141.
- [10] C. B. Fitzgerald, M. Venkatesan, A. P. Douvalais, S. Huber, J. M. D. Coey and T. Bakas, Appl. Phys. Lett. 95 (2004) 7390-7392.
- [11] J. M. D. Coey, A. P. Douvalis, C. B. Fitzgerald and M. Venkatesan, Appl. Phys. Lett. 84 (2004) 1332-1334.
- [12] S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene and T. Venkatesan, Phys. Rev. Lett. 91 (2003) 077205.
- [13] L. M. Fang, X. T. Zu, Z. J. Li, C. M. Liu, L. M. Wang and F. Gao, J. Mater. Sci. Mater. Electron 19 (2008) 868-874.
- [14] A. Punnoose, J. Hays, V. Gopal and V. Shutthanandan, Appl. Phys. Lett. 85 (2004) 1559-1561.
- [15] A. Punnoose, J. Hays, A. Thurber, M. H. Engelhard, R. K. Kukkadapu, C. Wang, V. Shutthanandan and S. Thevuthsan, Phys. Rev. B 72 (2005) 054402.
- [16] H. Wang, Y. Yan, X. Du, X. Liu, K. Li and H. Jin, J. of App. Phys. 107 (2010) 103923.
- [17] A. Fakhim Lamrani, M. Belaiche, A. Benyoussef, A. El Kenz and E.H. Saidi, J. Magn. Magn. Mater. 06 (2011) 2982-2986.
- [18] S. J. Liu, C. Y. Liu, J. Y. Juang and H. W. Fang, J. Appl. Phys. 105 (2009) 013928-013928-4.
- [19] J. P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048-5079.
- [20] B. Khalil, H. Labrim, O. Mounkachi, B. Belhorma, A. Benyoussef, A. El Kenz, E. Ntsoenzok, J. Supercond. Nov. Mag. December 2011, DOI: 10.1007/s10948-011-1381-4.
- [21] H. Wang, Y. Yan, Y. S. Mohammed, X. Du, K. Li and H. Jin, J. Magn. Magn. Mater 321 (2009) 3114-3119.
- [22] J.E. Jaffe, J.A. Snyder, Z. Lin and A.C. Hess, Phys. Rev. B, Condens. Matter 62 (2000) 1660-1665.
- [23] M. Toyoda, H. Akai, K. Sato and H. Katayama-Yoshida: Physica B: Condens. Matter 376-377 (2006) 647-650.
- [24] H. Akai: <http://sham.phys.sci.osaka-u.ac.jp/kkr/>.
- [25] V. L. Mouruzzi, J. F. Janak and A. R. Williams: Calculated Properties of Metals. Pergamon, New York (1998).
- [26] A. A. Bolzan, C. Fong, B. J. Kennedy and C. J. Howard, Acta Crystallogr. B 53 (1997) 373-380.
- [27] O. Mounkachi, A. Benyoussef, A. El Kenz, E.H. Saidi and E.K. Hlil, J. Appl. Phys. 106 (2009) 093905-093905-6.
- [28] R. C. Jaffe and A. C. Hess, Phys. Rev. B: Condens. Matter 248 (1993) 7903-7909.

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Approximation and Self-Interaction-Corrected**

- [29] F. Trani, M. Caus, D. Ninno, G. Cantele and V. Barone, J. Phys.: Condens. Matter 2 (2008) 804.
- [30] E. L. Peltzer y Blanca, A. Svane, N. E. Christensen, C. O. Rodrigues, O. M. Cappannini and M. S. Moreno, Phys. Rev. B 48 (1993) 15712-15718.
- [31] M. S. Park and B. I. Min, Phys. Rev. B 68 (2003) 224436.
- [32] K. Sato, P. H. Dederichs, H. Katayama Yoshida and J. Kudrnovsky, J. Phys.: Condens. Matter 16 (2004) S5491-S5497.
- [33] X. L. Wang, Z. X. Dai and Z. Zeng, J. Phys.: Condens. Matter 20 (2008) 045214.
- [34] X. L. Wang, Z. Zeng, X. H. Zheng and H. Q. Lin, J. of Appl. Phys. 101 (2007) 09H104-09H104-3.
- [35] C. Ke, W. Zhu, J. S. Pan, Z. Yang, Z. P. Li, L. Wang, J. Alloys and Compounds 509 (2011) 5008-5011.