RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

Rh polarization in ultrathin Rh layers on Fe(001)

A. Chouairi and H. Dreyssé
Laboratoire de Physique du Solide, Université de Nancy I, Boîte Postale 239, Vandoeuvre-les-Nancy, France

H. Nait-Laziz and C. Demangeat
Institut Physique Chimie Matériaux de Strasbourg, UMR46, Université Louis Pasteur, 67070 Strasbourg, France

(Received 3 June 1993)

We discuss the origin of the Rh polarization at the interface with a semi-infinite Fe(001) crystal obtained through spin-resolved valence-band and core-level spectroscopy. Due to the fact that it is not yet known how Rh grows on Fe(001), we discuss different epitaxial arrangements of Rh atoms on Fe(001), i.e., not only the usual fcc and bcc configurations but also face-centered tetragonal (fct) and body-centered tetragonal (bct) configurations which conserve the atomic volume. The fcc and bcc configurations do not agree with the experimental results because the polarization of the Rh is long ranged for fcc and too small for bcc. fct and bct configurations appear to be more favorable. Moreover, in all cases investigated an oscillatory polarization of the Rh atoms has been obtained.

During the last few years, intensive research work has been done in order to study artificial materials, where at least one component has bulk magnetic properties. Promising technological applications are one motivation. These studies are also of fundamental interest to try to understand atomic engineering. In such materials, for appropriate conditions, a transition metal which is usually paramagnetic in the fully symmetrical bulk geometry may present magnetic properties when the symmetry is reduced. Rh, which is isoelectronic to Co, is a good candidate to display such properties. Controversial results have been reported for the Rh/Ag(001) system. Many calculations show that Rh and Ru as monolayers on Ag(001) are magnetic. The most sophisticated full-potential-linearized-augmented-plane-wave method (FLAPW) calculations[1,2] display magnetic moments for Rh and Ru, but not for Pd. Other first-principles calculations[3–5] based on the local density approximation have also obtained similar results. Tight-binding calculations on the other hand have shown that the Rh monolayer on Ag is ferromagnetic[6,7] whereas Pd is not.[8] All these calculations lead to the conclusion that the Ru and Rh monolayers on Ag(001) are magnetic whereas Pd on Ag(001) is nonmagnetic. When the number of the overlayers on Ag(001) increases, the values of the magnetic moments of Ru and Rh decrease,[6,9] whereas for Pd surprisingly enough of a magnetic moment appears in the case of two or three Pd layers, for both free-standing[10] slabs as for overlayers on Ag(001).[6] This result obtained through the tight-binding approach has been recently confirmed by FLAPW calculations.[9] However, surface magneto-optic Kerr effect measurements for Pd/Ag(001) (Ref. 11) and Rh/Ag(001) (Ref. 12) do not show any onset of magnetism whereas the splitting of the 4*s* levels observed for thin coverage of Rh on Ag(001) were explained as due to a magnetic polarization.[13]

For a very thin film of Rh grown on a magnetic substrate, a polarization on the Rh atoms is expected: this has been obtained in the case of an Fe substrate.[14] Also Pd atoms appear to be magnetic at the interface with Fe.[15,16] This Rh magnetism can be, *a priori*, due to three reasons: (i) Moruzzi and Marcus[17] have shown that, in bulk transition metals, a magnetic moment can appear when the lattice parameter increases. If Rh grows epitaxially on Fe(001) with its bulk fcc structure it increases its lattice parameter. However, the lattice mismatch between the Rh and Fe interface is not enough to induce polarization in the Rh overlayer; (ii) the *d*-*d* hybridization between the *d* orbitals of Rh and Fe at the interface induces a polarization on the Rh atoms: this is usually a short-range polarization as has been shown in the case of the Fe/Pd interface;[16] (iii) a simple rule relates the magnetic moment of a given atom to its environment: the lower the coordination number, the higher the magnetic moment. This rule is true for Ru and Rh (Refs. 6 and 9) but is not valid in the case of Pd,[6,9,10] where the Pd monolayer which has the lowest coordination number of all the slabs is nonmagnetic whereas a bilayer is magnetic. This is due to the fact that the atomic configuration of atomic Pd is $4d^{10}5s^0$ so that no magnetic moment is present. Consequently, experimentalists have tried to put paramagnetic transition metals on substrates with a larger lattice constant (noble metals) in order to test the results of Moruzzi and Marcus.[17] Up to now, no clear trend has appeared. Also, the coordination number rule cannot be directly applied to transition-metal slabs which are paramagnetic in the bulk form. Only the *d*-*d* hybridization between a magnetic transition metal and a paramagnetic one seems to give experimentally a clear trend towards magnetism. In this paper we develop a theoretical approach where the three contributions are clearly discriminated.

The crystallographic structure of epitaxial films is not always clearly characterized. On a bcc substrate, two different types of structures can be considered: bcc-like with the substrate lattice parameter equal to a_{Fe} or fcc-like with a lattice parameter of $\sqrt{2}a_{\mathrm{Fe}}$. *A priori* relaxation perpendicular to the interface plane should be considered and tetragonal structures are expected. In a recent paper Kachel *et al.*[14] studied very thin Rh films on

Fe(001). These authors showed the existence of ferromagnetic order and the growth has been reported to be not a perfect layer-by-layer one. The Rh atomic arrangement has not been given. However, in the case of Pt on Fe(001), body-centered tetragonal structures have been observed.[18] By computing the magnetic moments distribution for fcc-like and bcc-like Rh films, we found that these two crystalline structures induce completely different magnetic properties: a long-range polarization for fcc structure and a very short one for bcc.

At first we determine the electronic and magnetic properties of the ground-state ($T = 0$ K) for the $(\mathrm{Rh})_n/\mathrm{Fe}(001)$ system through a Hubbard tight-binding Hamiltonian.[16] In this type of calculation, the exchange integrals which link the local magnetic moment and the band splitting of the local density of states, play a major role. The exchange integral J_{Fe} of the Fe substrate has been fixed in order to recover the bulk Fe magnetic mo-

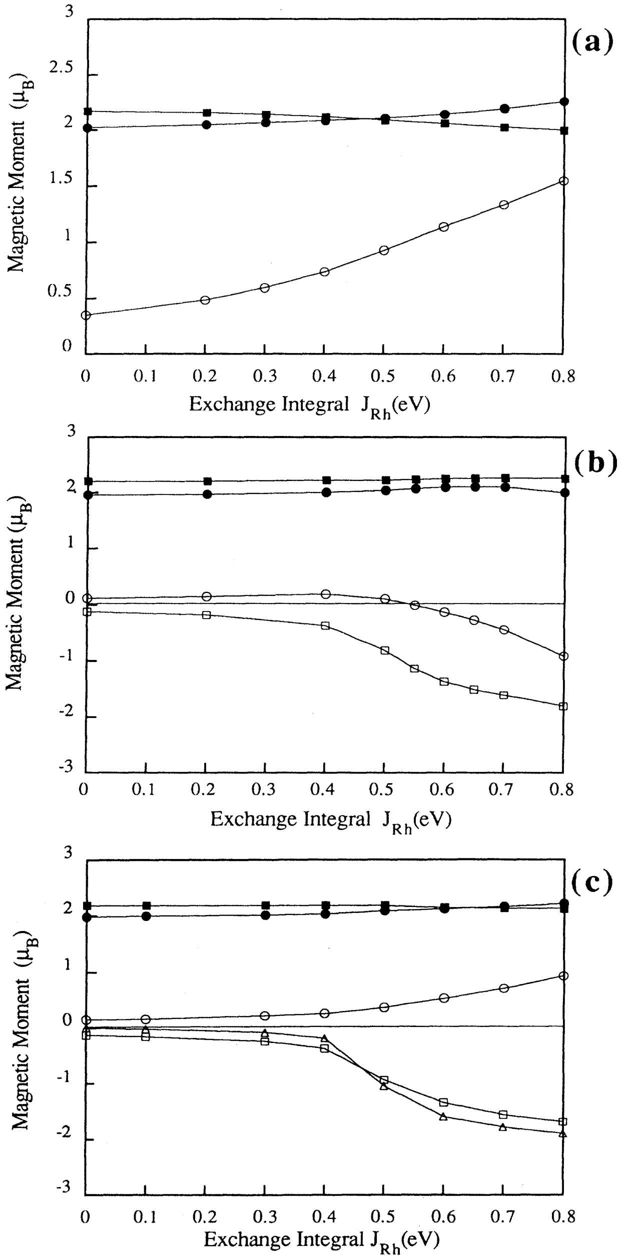

FIG. 1. Magnetic moment μ (in units of μ_B) per atom in terms of the exchange integral J_{Rh}, of rhodium for (a) a monolayer of fcc-like Rh adsorbed on Fe(001) semi-infinite substrate, (b) a bilayer of fcc-like Rh adsorbed on Fe(001) semi-infinite substrate, and (c) a triple layer of fcc-like Rh adsorbed on Fe(001) semi-infinite substrate. ■: $(\mathrm{Fe})_{I-1}$; ●: $(\mathrm{Fe})_I$; ○: $(\mathrm{Rh})_I$; □: $(\mathrm{Rh})_{I+1}$; △: $(\mathrm{Rh})_{I+2}$.

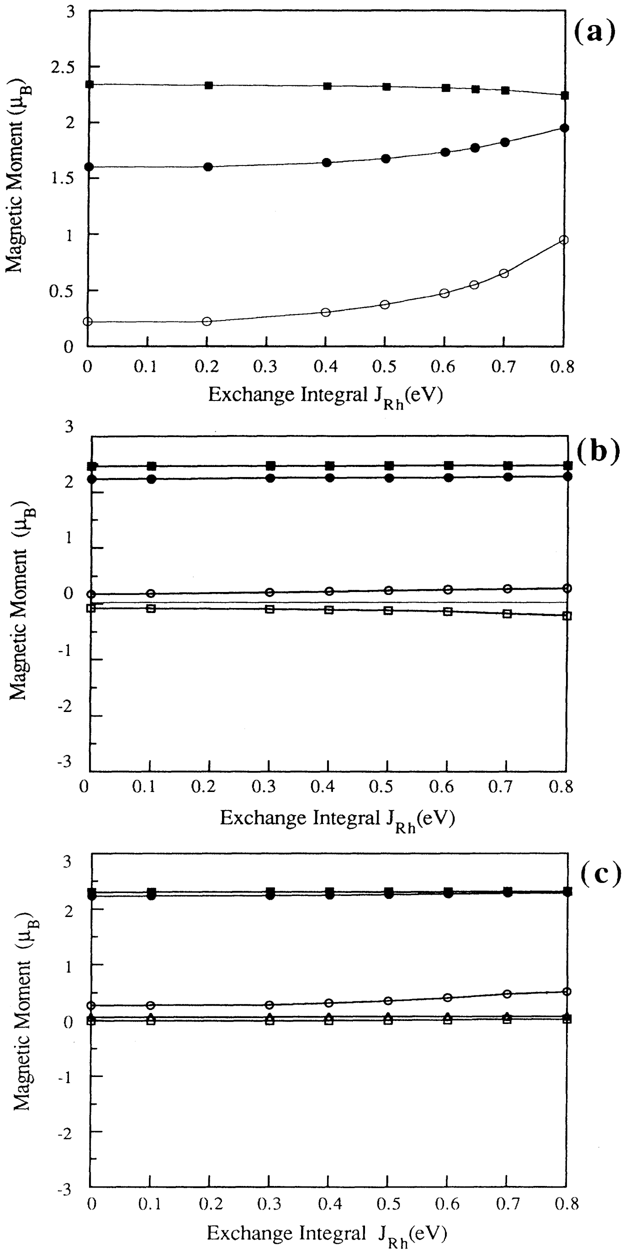

FIG. 2. Magnetic moment μ (in units of μ_B) per atom in terms of the exchange integral J_{Rh}, of rhodium for (a) a monolayer of bcc-like Rh adsorbed on Fe(001) semi-infinite substrate, (b) a bilayer of bcc-like Rh adsorbed on Fe(001) semi-infinite substrate, and (c) a triple layer of bcc-like Rh adsorbed on Fe(001) semi-infinite substrate. ■: $(\mathrm{Fe})_{I-1}$; ●: $(\mathrm{Fe})_I$; ○: $(\mathrm{Rh})_I$; □: $(\mathrm{Rh})_{I+1}$; △: $(\mathrm{Rh})_{I+2}$.

ment. For Rh, however, the value of J_{Rh} is not known: from a linear muffin-tin orbital calculation, Christensen *et al.*[19] indicate a value of $J_{\mathrm{Rh}}=0.60$ eV. According to Stollhoff, Oles, and Heine,[20] this value is overestimated by a factor of 20% due to the partial neglect of spin correlations in the local density approximation. This leads to a value of 0.50 eV for the exchange integral J_{Rh}. Nevertheless, we prefer to plot the magnetic moments of the Rh versus J_{Rh}. This will help us to discriminate between the three contributions leading to the polarizatoin at the Rh films.

In Fig. 1, we report the spin polarization of the $(\mathrm{Rh})_n$ film ($n=1,3$) on Fe(001) in the fcc crystallographic phase. For this geometry the Rh lattice parameter ($a=4.06$ Å) is larger than the bulk Rh value ($a_{\mathrm{bulk}}^{\mathrm{Rh}}=3.80$ Å). This increase of the Rh interatomic distance is, *a priori,* favorable to an onset of magnetism.[17,21] Thus it is not surprising to observe that for $J_{\mathrm{Rh}} \geq 0.45$ eV, a noticeable polarization of the Rh atom occurs. Furthermore the shape of the curve of the Rh magnetic moment indicates the contributions for the magnetism: when $J_{\mathrm{Rh}} \rightarrow 0$, a residual magnetic moment larger than $0.1\mu_B$ is already present: this contribution is due to d-orbital hybridization at the Fe/Rh interface. Thus by substracting this contribution, the intrinsic geometric effect occurs for $J \geq 0.40$ eV for $n=2$ and 3 and for a smaller value of J for the Rh monolayer. In fact, this geometric effect (or coordination rule effect) is directly observed for Rh atoms not at the interface with Fe(001).

Thus we can conclude that for a fcc-like Rh thin film on Fe(001), the magnetism is intrinsic, due to geometry of the film. Free-standing Rh slabs, with the lattice parameter of iron, have also been studied using the same theoretical framework.[22] The threshold value for the onset of magnetism has been found to be larger than the value deduced for the $(\mathrm{Rh})_n$/Fe(001) semi-infinite crystals. The presence of the magnetic substrate favors intrinsic magnetism. Using a FLAPW formalism, Kachel *et al.*[14] have computed the magnetic moment of Rh monolayer without relaxation. The value found by this *ab initio* calculation ($0.82\mu_B$) is in complete agreement with our calculation, i.e., 0.9 μ_B obtained in the case of fcc monolayer of Rh on Fe(001).

In Table I, we report the magnetic moment distribution for the fcc-like $(\mathrm{Rh})_n$/Fe(001) system for $n=1-6$ and for $J_{\mathrm{Rh}}=0.50$ eV; the nonrelaxed case where Rh has a perfect fcc arrangement and the so-called relaxed case (fct) where the distances between the planes parallel to the Rh/Fe interface are equally contracted in order to recover the bulk Rh atomic volume (this contraction is -18%).

For the perfect fcc-type Rh arrangement various comments can be made:

(1) A unique solution has been found for a given value of J_{Rh}.

(2) At the Rh-Fe interface, the Fe-Rh magnetic coupling is systematically ferromagnetic.

(3) The free-surface Rh atoms bear, in absolute value, the highest magnetic moment.

(4) The second and the third plane from the free surface are always antiferromagnetically coupled (except for $n=6$).

(5) The Rh interface plane is always antiferromagnetically coupled to the next Rh plane.

Let us mention that point (4) has already been found in a numerical determination of the Rh(001) magnetic moments: for a value of J_{Rh} chosen in order to have a surface magnetic moment and no bulk magnetic moment ($0.5 < J_{\mathrm{Rh}} < 0.6$ eV), all planes parallel to the (001) surface have been found ferromagnetically coupled, expect for the second and the third plane.[23]

By taking into account the relaxation of the Rh(001) planes (Table I) the magnetic moments are found in general to be lowered. The magnetic polarization is now short ranged. We report in Fig. 2 the magnetic moment distribution for bcc-like $(\mathrm{Rh})_n$ film on Fe(001) for $n=1,3$. Clearly no intrinsic magnetism occurs, only a small polarization is induced by the d-orbital hybridization at the Fe/Rh interface. For this geometric arrangement, the Rh-Rh distance (2.49 Å) is contracted compared to the bulk value. So in order to recover the bulk atomic volume, we have considered an outward relaxation of 5.4%. As can be inferred from Table II, this plane contraction is favorable for the magnetism: Rh atoms now display a noticeable magnetic moment.

For the monolayer of Rh on Fe(001), a decrease of the

TABLE I. Magnetic moment distribution for fcc- and fct-like $(\mathrm{Rh})_n$ ($n=1,2,\ldots,6$) layers adsorbed on Fe(001) for $J_{\mathrm{Rh}}=0.50$ eV. The index I stands for atoms at the Rh/Fe interface.

	Structure	$(\mathrm{Fe})_{I-1}$	$(\mathrm{Fe})_I$	$(\mathrm{Rh})_I$	$(\mathrm{Rh})_{I+1}$	$(\mathrm{Rh})_{I+2}$	$(\mathrm{Rh})_{I+3}$	$(\mathrm{Rh})_{I+4}$	$(\mathrm{Rh})_{I+5}$
$(\mathrm{Rh})_1$/Fe(001)	fcc	2.08	2.10	0.90					
	fct	2.23	1.63	0.56					
$(\mathrm{Rh})_2$/Fe(001)	fcc	2.22	2.03	0.12	−0.80				
	fct	2.39	1.96	−0.08	−0.93				
$(\mathrm{Rh})_3$/Fe(001)	fcc	2.18	2.08	0.36	−0.94	−1.04			
	fct	2.25	1.89	0.23	−0.15	−0.03			
$(\mathrm{Rh})_4$/Fe(001)	fcc	2.20	2.03	0.30	−0.38	0.05	0.43		
	fct	2.44	1.44	−0.04	−0.12	0.04	0.18		
$(\mathrm{Rh})_5$/Fe(001)	fcc	2.20	2.05	0.33	−0.45	−0.21	0.48	0.81	
	fct	2.33	1.86	0.25	−0.10	−0.02	0.02	0.06	
$(\mathrm{Rh})_6$/Fe(001)	fcc	2.19	2.05	0.37	−0.31	−0.12	0.08	0.27	0.41
	fct	2.30	1.85	0.24	−0.12	0.00	−0.20	0.02	0.15

TABLE II. Magnetic moment distribution for bcc- and bct-like $(\mathrm{Rh})_n$ ($n=1, 2, \ldots, 6$) layers adsorbed on Fe(001) for $J_{\mathrm{Rh}}=0.50$ eV. The index I stands for atoms at the Rh/Fe interface.

	Structure	$(\mathrm{Fe})_{I-1}$	$(\mathrm{Fe})_I$	$(\mathrm{Rh})_I$	$(\mathrm{Rh})_{I+1}$	$(\mathrm{Rh})_{I+2}$	$(\mathrm{Rh})_{I+3}$	$(\mathrm{Rh})_{I+4}$	$(\mathrm{Rh})_{I+5}$
$(\mathrm{Rh})_1$/Fe(001)	bcc	2.32	1.68	0.37					
	bct	2.21	2.15	0.66					
$(\mathrm{Rh})_2$/Fe(001)	bcc	2.47	2.25	0.23	−0.13				
	bct	2.27	2.20	−0.12	−0.80				
$(\mathrm{Rh})_3$/Fe(001)	bcc	2.31	2.25	0.35	0.00	0.06			
	bct	2.22	2.14	0.27	−0.28	−0.16			
$(\mathrm{Rh})_4$/Fe(001)	bcc	2.34	2.14	0.35	−0.01	0.00	−0.02		
	bct	2.29	2.14	0.23	−0.19	0.05	0.15		
$(\mathrm{Rh})_5$/Fe(001)	bcc	2.35	2.18	0.38	0.00	0.04	0.00	0.00	
	bct	2.29	2.16	0.21	−0.22	−0.05	0.03	−0.08	
$(\mathrm{Rh})_6$/Fe(001)	bcc	2.29	2.16	0.35	0.01	0.04	0.02	0.00	0.00
	bct	2.28	2.15	0.21	−0.24	−0.05	0.01	−0.08	−0.18

magnetic moments of both Fe and Rh atoms at the interface is obtained for the fct configuration compared to the fcc structure. This results from the fact that the Rh-Rh distances are smaller in the fct configuration (atomic volume) compared to an increase of 18% in the fcc phase. Also, the distance between Fe and Rh at the interface is given by $(a_{\mathrm{Fe}}+a_{\mathrm{Rh}})/4$ whereas it is $(a_{\mathrm{Fe}}+\sqrt{2}a_{\mathrm{Fe}})/4$ for the fcc phase. In general, the magnetic moments of Fe at the Fe/Rh interface are lower in the fct phase and the polarization of Rh at this interface is not always ferromagnetically aligned to Fe as it is in the case for fcc. For the Rh bilayer on Fe, the Rh layers have negative polarization in the fct configuration. For thickness greater than $n=2$, the magnetic moments of the Rh planes are found with a much smaller polarization in the fct phase compared to the fcc structure. This is directly related to the fact that the Rh-Rh distance is smaller for the fct configuration.

In this paper we have discussed the polarization of Rh atoms adsorbed on an Fe(001) substrate. Because the location of these Rh atoms is not yet well determined we have considered epitaxial growth with fcc and bcc structure with the lattice parameter of bulk Fe. Neither of these configurations are in agreement with the polarization reported by Kachel *et al.*[14] Therefore we have considered epitaxial growth polarization which conserves the atomic volume, i.e., fct and bct structures. In both cases the Rh polarization displays a similar trend which seems to be in good agreement with Kachel's experimental findings.[14] Nevertheless, the Fe polarization at the Fe/Rh interface remains much higher in the bct crystallograpahic phase than in the fct structure. This is, however, not really surprising if we remember that fcc iron is not a good magnetic system.[19] The main conclusions are (i) the noticeable polarization of the Rh atom up to the Rh bilayer; (ii) the fact that, as in the case of Pd atoms on Fe(001) (Ref. 16) an oscillation of the Rh polarization is present. We are awaiting more detailed structural investigations of the growth of Rh on Fe(001).

---

[1] S. Blügel, Europhys. Lett. **18**, 257 (1992).
[2] R. Wu and A. J. Freeman, Phys. Rev. B **45**, 7222 (1992).
[3] O. Eriksson, R. C. Albers, and A. M. Boring, Phys. Rev. Lett. **66**, 1351 (1991).
[4] Ming J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **42**, 2874 (1990).
[5] Ming J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **43**, 4007 (1991).
[6] A. Mokrani, H. Dreyssé, S. Bouarab, and C. Demangeat, J. Magn. Magn. Mater. **113**, 201 (1992).
[7] P. Rennert, W. Hergert, C. Demangeat, and H. Dreyssé, J. Magn. Magn. Mater. (to be published).
[8] H. Dreyssé, A. Mokrani, S. Bouarab, and C. Demangeat, Surf. Sci. **251/252**, 41 (1991).
[9] S. Blügel, *Europhysics Conference Abstracts*, edited by G. Thomas (European Physical Society, Petit-Lancy, Switzerland, 1993), Vol. 17A, p. 1200.
[10] S. Bouarab, C. Demangeat, A. Mokrani, and H. Dreyssé, Phys. Lett. A **41**, 103 (1990).
[11] R. L. Fink, C. A. Ballentine, J. L. Erskine, and J. Araya Rochet, Phys. Rev. B **41**, 10 175 (1990).
[12] G. A. Mulhollan, R. L. Fink, and J. L. Erskine, Phys. Rev. B **44**, 2393 (1991).
[13] H. Li, S. C. Wu, D. Tian, Y. S. Li, J. Quinn, and F. Jona, Phys. Rev. B **47**, 6630 (1993).
[14] T. Kachel, W. Gudat, C. Carbone, E. Vescovo, S. Blügel, U. Altkemper, and W. Eberhardt, Phys. Rev. B **46**, 12 888 (1992).
[15] Z. Celinski and B. Heinrich, J. Magn. Magn. Mater. **99**, L25 (1991).
[16] H. Nait-Laziz, S. Bouarab, C. Demangeat, A. Mokrani, and H. Dreyssé, J. Magn. Magn. Mater. **118**, 365 (1993).
[17] V. L. Moruzzi and P. M. Marcus, Phys. Rev. B **39**, 471 (1989).
[18] G. W. R. Leibbrandt, R. Van Wijk, and F. H. P. M. Habraken, Phys. Rev. B **47**, 6630 (1993).
[19] N. E. Christensen, O. Gunnarsson, O. Jepsen, and O. K. Andersen, J. Phys. (Paris) Colloq. **49**, C8-17 (1988).
[20] G. Stollhoff, A. M. Oles, and V. Heine, Phys. Rev. B **41**, 7028 (1990).
[21] D. Stoeffler and H. Dreyssé, Solid State Commun. **79**, 645 (1991).
[22] A. Chouairi, Ph.D. thesis, University of Nancy, 1993 (unpublished).
[23] A. Mokrani and H. Dreyssé (unpublished).