Calculated electronic structure and x-ray magnetic circular dichroism of CrO_2

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Abstract

A theoretical study of the electronic structure and magnetic properties of the half-metallic ferromagnet CrO_2 is performed by means of the relativistic full-potential linear muffin-tin orbital method within the generalized gradient approximation (GGA) to the exchange correlation potential. The calculated spin and orbital magnetic moments at the chromium site agree well with existing experimental and theoretical results. It is found that the easy magnetization is along the [001] axis in agreement with experiment, which is confirmed by a noticeable anisotropy between the calculated chromium $L_{2,3}$ x-ray magnetic circular dichroism (XMCD) spectra for the [100] and [001] quantization directions. Furthermore, the oxygen K edge XMCD spectrum clearly shows an induced magnetism at the oxygen site, in agreement with experiment. The XMCD sum-rule-computed spin and orbital magnetic moments from the experimental spectra are close to the self-consistent results and are in good agreement with most experimental results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Chromium dioxide is the only stoichiometric binary oxide that is a ferromagnetic metal and also the simplest and best studied half-metal [1]. In recent years, magneto-electronic devices such as spin valve field sensors and magnetic random access memories have emerged, where both the charge and spin of electrons are exploited using spin-polarized currents and spin-dependent conduction [2, 3]. The performance of such magneto-electronic devices depends critically on the substantial spin polarization of the ferromagnetic components. CrO_2 attracts specific interest as the only compound experimentally reported so far to possess 100% spin polarization. The half-metallic band structure of CrO_2 was confirmed

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by several experimental techniques such as Andreev reflection, superconducting tunnelling, photoemission, point-contact magnetoresistance, x-ray absorption, resonant scattering and Raman spectroscopy [4–13].

Half-metallic ferromagnetic materials appear as potential spintronics candidates and a lot of work is in progress to synthesis magnetic oxides such as CrO_2, Fe_3O_4 and Sr_2FeMoO_6 which are found to posses a high Curie temperature (T_c). Recently Sr_2CrReO_6 a chromium based double perovskite was found to have a T_c of 635 K, which is the highest among the double perovskite family [14]. Numerous theoretical works are available for CrO_2 explaining the electronic structure, bonding, optical and magneto-optical properties and magneto-crystalline anisotropy (MCA) [15–24]. Because of the uniaxial crystal structure, CrO_2 is expected to have a large magnetic anisotropy which makes it the favoured material for magneto-optical recording. Recently it has been shown that the low-temperature experimental data were reproduced well by the local spin density approximation (LSDA) without the need for the Hubbard interaction U, confirming that the ordered phase of CrO_2 is weakly correlated [24].

Circular dichroism-type spectroscopy became a powerful tool in the study of the electronic structure of magnetic materials [25, 26]. It has been demonstrated by Weller *et al* [27] that x-ray magnetic circular dichroism (XMCD) is also a suitable technique for determining the MCA at an atomic scale, via the determination of the anisotropy of the orbital magnetic moment for each shell and site. Recently, the angle resolved XMCD technique has been applied by Goering *et al* [28, 29, 31] for a wide range of temperature to investigate the anisotropies of orbital moments l_z and the magnetic dipole term t_z of chromium atoms in epitaxial CrO_2 films grown on a TiO_2 substrate. From their XMCD studies they found large anisotropies of l_z and t_z, where the latter was derived from the semi-empirical van der Laan's method of moment analysis [32]. In addition, x-ray absorption spectroscopy (XAS) using circularly polarized radiation probes element-specific magnetic properties of compounds using the XMCD sum rules [33–35].

Theoretical understanding of XMCD for magnetic material is not an easy task, and several *ab initio* calculations have been attempted for transition metals and rare-earth compounds [36–43] with limited success. The L_2 and L_3 edges involving electronic excitations of the 2p core electrons towards the s and d conduction states have attracted much attention due to the dependence of the XMCD spectra on the exchange-splitting and the spin–orbit coupling (SOC) of both initial core levels and final conduction states. Though there are several theoretical studies of the electronic and magnetic properties of CrO_2, we are not aware of any published work concerning the XMCD spectra except for the atomic calculations in a crystal-field symmetry of van der Laan and Thole concerning the Cr^{2+} and Cr^{3+} ions and other 3d transition-metal ions [44]. In these atomic calculations the XMCD of the Cr^{4+} state which is supposed to represent chromium in CrO_2 was not investigated. Parallel to our study, Baadji and co-workers [45] are investigating the effect of the Hubbard interaction on the magnetic properties and XMCD spectra of CrO_2 using the full-potential linear augmented plane wave (FPLAPW) method.

In the present work we studied the $L_{2,3}$ and K edge XAS and XMCD at the chromium and oxygen sites of CrO_2, respectively, using the relativistic full-potential linear muffin-tin orbital (FPLMTO) method. In section 2 we briefly present our method, and in the third section we discuss the density of states and magnetic moments. In section 4 we calculate the XAS and XMCD spectra of CrO_2 and compare the results with the experimental results.

2. Method of calculation

The electronic structure calculations were performed using the all-electron FPLMTO method [46] including the SOC directly in the Hamiltonian. The exchange–correlation potential
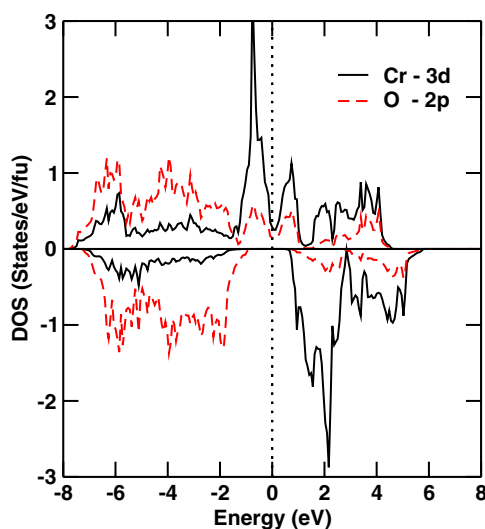
Figure 1. Calculated partial Cr 3d and O 2p density of states of CrO$_2$. The dotted line represents the Fermi level.

is parametrized using the generalized gradient approximation (GGA) [47], and the spherical-harmonic expansion of the potential was performed up to $l_{max} = 6$. We used a double basis set so that each orbital is described using two kinetic energy parameters. The basis set consists of the chromium 4s, 4p and 3d orbitals and oxygen 2s and 2p orbitals.

The calculations are performed using the experimental structure and atomic positions, i.e. the rutile structure with space group symmetry $P4_2/mmm$ and with cell parameters $a = b = 4.419$ Å, $c = 2.912$ Å [48]. The radii of the muffin-tin spheres used for the chromium and oxygen are 2.0 and 1.5 atomic units, respectively. To calculate the magnetic anisotropy we calculated the ground state total energy only for the [001] and the [100] magnetization directions. Integration in the Brillouin zone (BZ) is performed using the tetrahedron method [49]. We used 1100 and 1200 irreducible **k** points in the BZ for the magnetization along the [001] and the [100] directions, respectively. Note that to avoid numerical errors one has to use the same **k** BZ grid for both spin quantization axes and let the symmetry of the crystal in the presence of the SOC decide the number of irreducible **k** points.

The theoretical XAS and XMCD spectra were calculated using a method described elsewhere [38]. This method was found to be successful in reproducing the experimental XAS and XMCD spectra of several transition-metal compounds [38, 42, 43].

3. Electronic structure

The electronic structure of CrO$_2$ has been extensively reported in the literature [15–22, 24] so in this section we present and discuss only the density of states and compare it with earlier results.

Figure 1 shows the density of states (spin up and spin down) of Cr 3d and O 2p states. For the majority spin, the Fermi level lies near a local minimum of the Cr 3d t$_{2g}$ band with the DOS at the Fermi level. For the minority spin, the Fermi level falls in a gap of 1.34 eV which is in agreement with earlier results [15, 18–21]. The calculated exchange splitting between the majority and the minority spin main peaks of the chromium 3d t$_{2g}$ band is found

to be 2.3 eV. A similar splitting of 2.5 eV has been found using the FPLAPW method [20], and a splitting of 2.3 eV in a recent FPLMTO calculation [21]. All the exchange splittings calculated within the LSDA or GGA are too small when compared with the measured large splitting of about 5 eV between the main peaks in the occupied and the empty Cr 3d DOS obtained in photoemission [50]. It is interesting to note that half-metallic gap persists even in the presence of SOC, despite the fact that the SOC destroyed the half-metallicity in many Heusler alloys, dilute magnetic semiconductors, zinc blende type transition-metal pnictides and double perovskites [51, 52].

The calculated spin and orbital magnetic moments along the [001] axis of magnetization are found to be 1.99 μ_B and -0.045 μ_B per atom at the chromium site and -0.08 μ_B and -0.0017 μ_B/atom at the oxygen site. The calculated spin magnetic moments of chromium and oxygen are slightly larger than the recent LSDA FPLMTO results of Jeng and Guo [21]. The GGA, used here, has a tendency to increase the spin moment. Nevertheless our orbital magnetic moments at the chromium and oxygen sites compare well with the recent FPLAPW calculation [23]. From the above results it can be seen that the orbital magnetic moment of chromium is almost quenched and is antiparallel to the spin moment, which is consistent with Hund's rule for 3d shells that are less than half filled. A similar quenched orbital magnetic moment for chromium has been recently reported in the double perovskite Sr_2CrReO_6 [52]. The orbital magnetic moment of the oxygen atom is parallel to the spin moment because the O 2p shell is more than half filled. The calculated spin moment of oxygen is antiparallel to the spin moment of chromium, and hence the chromium and oxygen are coupled antiferromagnetically. The calculated orbital magnetic moments of chromium and oxygen are slightly lower than those obtained from the experimental XMCD by Huang and co-workers [53].

For the oxygen atom the spin moment is too low when compared with the value estimated by Goering *et al* [28]. However, it was recently shown [23] that a calculation using a Hubbard interaction $U = 3$ eV produced a spin moment of 0.1 μ_B, a factor of four times smaller than the value obtained by Goering *et al* [28]. In order to find the easy axis of magnetization we have performed self-consistent calculations along the [001] and [100] magnetization directions. Our calculations show that the easy magnetization direction is along the [001] axis in agreement with available experimental data [31, 55–58].

4. X-ray absorption and magnetic circular dichroism

In this section we calculate, analyse and compare the XMCD spectra with experiment. XMCD spectroscopy is not only element specific but also orbital specific, and hence the electronic states of the 3d transition metals can be probed by K, $L_{2,3}$, $M_{2,3}$ x-ray absorption or emission spectroscopy. The dichroism at the L_2 and L_3 edges is influenced by the strong SOC of the initial 2p core states giving rise to a pronounced dichroism in comparison with that at the K edge.

In figure 2, we present the $L_{2,3}$ XAS and XMCD spectra for chromium atoms for both the [100] and [001] magnetization directions. We convoluted our theoretical spectra using a Lorentzian and Gaussian width both of 0.5 eV. The Gaussian broadening represents the experimental resolution while the Lorentzian one corresponds to the width of the core hole. The calculated total absorption spectra corresponding to the chromium $L_{2,3}$ edge is shown in the upper part of the figure. We have scaled our spectra so that the experimental and theoretical L_3 peaks in the absorption spectra have the same intensity. The energy difference between the L_3 and L_2 peaks is given by the spin–orbit splitting of $p_{1/2}$ and $p_{3/2}$ core states of about 8.65 eV, in good agreement with the experimental value of 8.2–8.6 eV [54]. As far the absorption spectra are concerned the present theory represents well the experimental features but underestimates
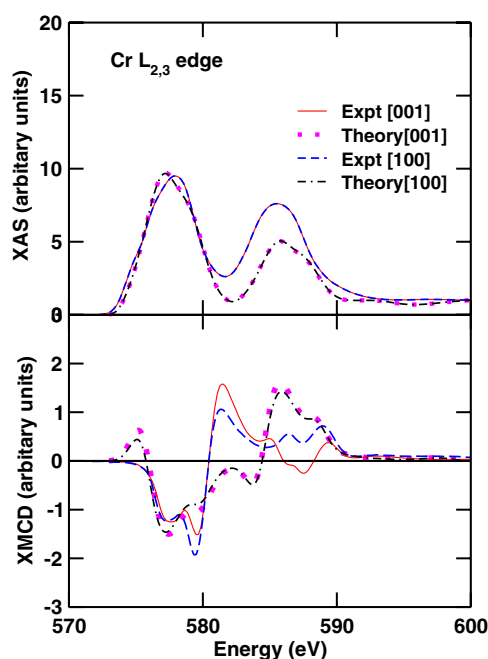
Figure 2. Calculated chromium L$_{2,3}$ XAS and XMCD spectra of CrO$_2$ for magnetization along the [100] and the [001] directions. The results are compared to the experimental spectra of [28, 30]. Note that only the first peak of the XAS is scaled to reproduce the experimental intensity and the deduced XMCD is directly compared to experiment.

the intensity of the L$_2$ peak. The calculated [100] and [001] XMCD spectra, presented in the lower part of the figure, show a noticeable anisotropy in qualitative agreement with experiment. It is surprising that the experimental XMCD anisotropy is quite pronounced, whereas it is only just noticeable in the absorption spectra (see upper plot of figure 2). The calculation seems to reproduce the different features in the experimental spectra but only at the qualitative level. The electron–hole interaction not taken into account in our calculation may considerably improve the agreement between the theory and the experiment. Nevertheless, the theory explains the two structures present in both L3 and L2 XMCD parts of the spectrum in terms of the two first peaks, respectively, in the spin-up and spin-down density of states just above the Fermi level. The theory fails to explain the negative XMCD present in the [001] polarization.

Using the XMCD sum rules we calculate the spin and orbital magnetic moment of the Cr 3d state, which are found to be 1.82 and -0.044 μ_B/atom, respectively, in good agreement with the values obtained from the self-consistent calculations. The calculations are presented in table 1 and compared to various experimental data. The spin and orbital magnetic moments obtained using the sum rules compare favourably with the LSDA values of Huang *et al* [53]. Despite the fact that the experimental study of Huang *et al* [53] could not uniquely define which part of the L$_{2,3}$ spectrum belongs to the L$_3$ or the L$_2$ edge, their measured spin moment is in good agreement with our calculation. In contrast, the chromium spin magnetic moment XMCD measurement of Goering and co-workers [28] produced a value of 1.2 μ_B which was too small, and their value of 2.4 μ_B, obtained by applying a spin correction to the spectra [54], is much higher (see table 1). Their orbital magnetic moment is also smaller than all calculated and measured values.
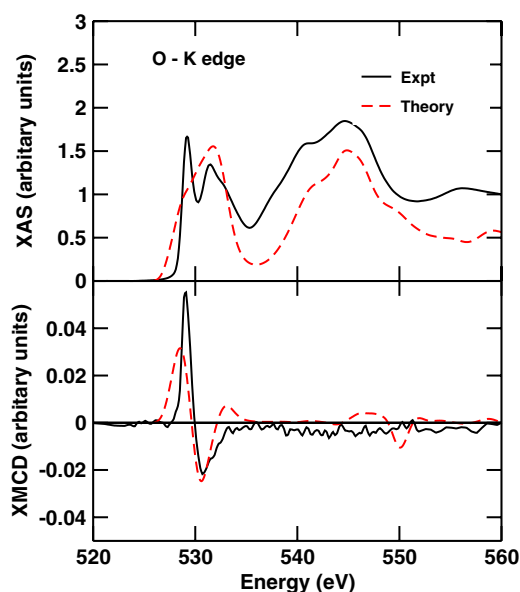
Figure 3. O K edge XAS and XMCD spectra of CrO_2 along the [001] magnetization axis. The experimental spectrum is taken from [28].

Table 1. Spin and orbital magnetic moments of chromium d states in μ_B per atom obtained using the sum rules (SR) and the self-consistent (SC) calculation with the magnetization along the [001] direction compared with available experimental results [28, 53, 54].

μ_s		μ_1		Experiment	
SR	SC	SR	SC	μ_s	μ_1
1.82	1.99	−0.044	−0.045	1.9 ± 0.1^a, 1.2^b, 2.4^c	-0.06 ± 0.02^a, -0.02^b

[a] Reference [53]; [b] Reference [28]; [c] Reference [54].

In figure 3 we show the oxygen K edge XAS and XMCD spectra along the [001] axis of magnetization. We used a similar broadening as that of the Cr $L_{2,3}$ for the oxygen K edge. The oxygen K edge spectrum mainly comes from excitation of the 1s state and is less intense when compared to the $L_{2,3}$ edge of chromium. The exchange splitting of the initial 1s core state has an extremely small value, therefore only the exchange and spin–orbit splitting of the final 2p state is responsible for the observed dichroism at the K edge. However, the present calculation reproduces fairly well the experimentally observed O K edge and XMCD spectra.

The oxygen orbital magnetic moment is almost quenched in the [100] axis, which is similar to the earlier theoretical results [21, 23] resulting in a weak intensity of the oxygen K edge in contrast to the experiments, which show the same angular dependency for the Cr 3d orbital projections and the O K edge XMCD.

5. Conclusions

In the present work we have carried out a theoretical study of the magnetic properties of CrO_2. The calculated half-metallic band structure of CrO_2 is in agreement with earlier studies. Our calculation confirms the *c*-axis to be the easy axis of magnetization. The calculated XAS and XMCD spectra of chromium $L_{2,3}$ and the oxygen K edge compare fairly well with the

experimental results. The L$_3$/L$_2$ branching ratio is higher when compared to the experiments which could be improved by including the 3d core–hole interaction. In addition the spin and orbital magnetic moments obtained from the sum rules are in good agreement with the self-consistent results and the experimental data. These latter results are surprising since it has always been believed that the sum rule applies only when the intermixing of the L$_2$ and L$_3$ XMCD spectra is small.

Acknowledgments

References

[1] Coey J M D and Venkatesan M 2002 *J. Appl. Phys.* **91** 8345
[2] Prinz G A 1995 *Phys. Today* **48** 58
[3] Daughton J M, Pohm A V, Fayfield R T and Smith C H 1999 *J. Phys. D: Appl. Phys.* **32** R169
[4] Ji Y, Strijkers G J, Yang F Y, Chein C L, Byers J M, Anguelouch A, Xiao G and Gupta A 2001 *Phys. Rev. Lett.* **86** 5585
[5] Parker J S, Watts S M, Ivanov P G and Xiong P 2001 *Phys. Rev. Lett.* **89** 196601
[6] Kämper K P, Schmitt W, Güntherodt G, Gambino R J and Ruf R 1987 *Phys. Rev. Lett.* **59** 2788
[7] Dedkov Y S, Fonine M, Konig C, Rudiger U, Guntherodt G, Senz S and Hesse D 2002 *Appl. Phys. Lett.* **80** 4181
[8] Coey J M D, Berkowitz A E, Balcells L I, Putris F F and Barry A 1998 *Phys. Rev. Lett.* **80** 3815
[9] Coey J M D and Sanvito S 2004 *J. Phys. D: Appl. Phys.* **37** 988
[10] Huang D J, Tjeng L H, Chen J, Chang C F, Wu W P, Chung S C, Tanaka A, Guo G Y, Lin H J, Shyu S G, Wu C C and Chen C T 2003 *Phys. Rev.* B **67** 214419
[11] Stagarescu C B, Su X, Eastman D E, Altmann K N, Himpsel F J and Gupta A 2000 *Phys. Rev.* B **61** R9233
[12] Kurmaev E Z, Moewes A, Butorin S M, Katsnelson M I, Finkelstein L D, Nordgren J and Tedrow P M 2003 *Phys. Rev.* B **67** 155105
[13] Iliev M N, Litvinchuk A P, Lee H G, Chu C W, Barry A and Coey J M D 1999 *Phys. Rev.* B **60** 33
[14] Kato H, Okuda T, Okimoto Y, Tomioka Y, Takenoya Y, Ohkubo A, Kawasaki M and Tokura Y 2002 *Appl. Phys. Lett.* **81** 328
[15] Schwarz K 1986 *J. Phys. F: Met. Phys.* **16** L211
[16] Sorantin P I and Schwarz K 1992 *Inorg. Chem.* **31** 567
[17] Uspenskii Yu A, Kulatov E T and Halilov S V 1996 *Phys. Rev.* B **54** 474
[18] Lewis S P, Allen P B and Sasaki T 1997 *Phys. Rev.* B **55** 10253
[19] Korotin M A, Anisimov V I, Khomskii D I and Sawatzky G A 1998 *Phys. Rev. Lett.* **80** 4305
[20] Mazin I I, Singh D J and Ambrosch-Draxl C 1999 *Phys. Rev.* B **59** 411
     Mazin I I, Singh D J and Ambrosch-Draxl C 1999 *J. Appl. Phys.* **85** 6220
[21] Jeng H T and Guo G Y 2002 *J. Appl. Phys.* **92** 951
[22] Kuneś J, Novák P, Oppeneer P M, König C, Fraune M, Rüdiger U, Güntherodt G and Ambrosch-Draxl C 2002 *Phys. Rev.* B **65** 165105
[23] Komelj M, Ederer C and Fähnle M 2004 *Phys. Rev.* B **69** 132409
[24] Toropova A, Kotlair G, Savrasov S Y and Oudovenko V S 2005 *Phys. Rev.* B **71** 172403
[25] Bagus P S, Pacchioni G and Parmigiani P (ed) 1995 *Core Level Spectroscopies for Magnetic Phenomenon: Theory and Experiment* (New York: Plenum)
[26] Ebert H and Schütz G (ed) 1996 *Spin–Orbit Influenced Spectroscopies of Magnetic Solids* (*Lecture Notes in Physics* vol 466) (Heidelberg: Springer)
[27] Weller D, Stöhr J, Nakajima R, Carl A, Samant M G, Chappert C, Mégy R, Beauvillain P, Veillet P and Held G A 1995 *Phys. Rev. Lett.* **75** 3752
[28] Goering E, Bayer A, Gold S, Schütz G, Rabe M, Rüdiger U and Güntherodt G 2002 *Phys. Rev. Lett.* **88** 207203
[29] Goering E, Bayer A, Gold S, Schütz G, Rabe M, Rüdiger U and Güntherodt G 2002 *Eur. Phys. Lett.* **58** 906
[30] Goering E, private communication
[31] Gold S, Goering E, König C, Rüdiger U, Güntherodt G and Schütz G 2005 *Phys. Rev.* B **71** 220404

[32] van der Laan G 1997 *J. Phys.: Condens. Matter* **9** L259
[33] Thole B T, Carra P, Sette F and van der Lann G 1992 *Phys. Rev. Lett.* **68** 1943
[34] Carra P, Thole B T, Altarelli M and Wang X 1993 *Phys. Rev. Lett.* **70** 694
[35] van der Laan G 1998 *Phys. Rev.* B **57** 112
[36] Wu R, Wang D and Freeman A J 1993 *Phys. Rev. Lett.* **71** 3581
 Wu R and Freeman A J 1994 *Phys. Rev. Lett.* **73** 1994
[37] Ebert H 1996 *Rep. Prog. Phys.* **59** 1665
[38] Alouani M, Wills J M and Wilkins J W 1998 *Phys. Rev.* B **57** 9502
[39] Brouder C and Hikam M 1991 *Phys. Rev.* B **43** 3809
 Brouder C, Alouani M and Bennemann K H 1996 *Phys. Rev.* B **54** 7334
[40] Guo G Y 1998 *Phys. Rev.* B **57** 10295
[41] Ankudinov A and Rehr J J 1997 *Phys. Rev.* B **56** 1712
[42] Galanakis I, Ostanin S, Alouani M, Dreyssé H and Wills J M 2000 *Phys. Rev.* B **61** 599
 Galanakis I, Ostanin S, Alouani M, Dreyssé H and Wills J M 2000 *Phys. Rev.* B **61** 4093
[43] Galanakis I, Alouani M and Dreyssé H 2002 *J. Magn. Magn. Mater.* **242–245** 27
[44] van der Laan G and Thole B T 1991 *Phys. Rev.* B **43** 13 401
[45] Baadji N, Alouani M and Dreyssé H, unpublished
[46] Wills J M, Eriksson O, Alouani M and Price O L 2000 *Electronic Structure and Physical Properties of Solids* ed H Dreyssé (Berlin: Springer)
[47] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[48] Porta P, Marezio M, Remeika J P and Dernier P D 1972 *Mater. Res. Bull.* **7** 157
[49] Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1763
 Lehmann G and Taut M 1972 *Phys. Status Solidi* **54** 469
[50] Tsujioka T, Mizokawa T, Okamoto J, Fujimori A, Nohra M, Takagi H, Yamaura K and Takano M 1997 *Phys. Rev.* B **56** R15509
[51] Dederichs P H, Popescu V and Ebert H 2004 *Phys. Rev.* B **69** 054424
[52] Vaitheeswaran G, Kanchana V and Delin A 2005 *Appl. Phys. Lett.* **86** 0325132005
[53] Huang D J, Jeng H T, Chang C F, Guo G Y, Chen J, Wu W P, Chung S C, Shyu S G, Wu C C, Lin H J and Chen C T 2002 *Phys. Rev.* B **66** 174440
[54] Goering E 2005 *Phil. Mag.* B **85** 2895
[55] Spinu L, Srikanth H, Gupta A, Li X W and Xiao G 2000 *Phys. Rev.* B **62** 8931
[56] Yang F Y, Chein C L, Ferrari E F, Li X W, Xiao G and Gupta A 2000 *Appl. Phys. Lett.* **77** 286
[57] Li X W, Gupta A and Xiao G 1999 *Appl. Phys. Lett.* **75** 713
[58] Miao G, Xiao G and Gupta A 2005 *Phys. Rev.* B **71** 094418