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Band theoretical investigation of substituted CrO_2 within the local density approximation

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Résumé. — Les effets de substitutions à différentes concentrations dans le réseau de CrO_2 sont examinés en supposant des configurations ordonnées. Pour ces études on utilise des calculs auto-cohérents de structure de bande basés sur l'approximation de la densité électronique locale. Les résultats montrent des spins opposés entre Cr et l'élément substituant $M = \text{Ir}, \text{Os}, \text{Pt}$. Suivant la nature de M et sa concentration, CrO_2 se transforme de ferromagnétique semi-métallique en un ferrimagnétique semi-métallique ou métallique.

Abstract. — The effects of substitutions at different concentrations within the lattice of CrO_2 are investigated assuming ordered configurations. For this purpose we use self-consistent band structure calculations based on the local spin density approximation. All results show an antiparallel spin alignment between host Cr and the substitutional $M = \text{Ir}, \text{Os}, \text{Pt}$. Depending on the nature of M and its concentration, CrO_2 transforms from a half metallic ferromagnet to a half-metallic or metallic ferrimagnet.

1. Introduction.

CrO_2 is a ferromagnetic oxide well known for its use in magnetic recording applications. Since its discovery by Michel and Bénard in the first decades of this century [1] much work has been devoted to the development of new preparation methods [2, 3] and to the study of its physical properties [4]. However its electronic structure is still a subject of controversy. From our recent investigations of the electronic and magnetic properties by using self-consistent band structure calculations (see [5] and the erratum published this issue) CrO_2 is predicted as a half metallic ferromagnet i.e. 100 % polarization of conduction electrons in the majority spin states and a

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2 eV band gap at minority spin states. These findings are in agreement with other authors' [6, 7]. However spin-resolved X-ray photoemission spectroscopy experiments on the layered material reveal a vanishing density of states at Fermi level and a 100 % polarization of the electrons 1 eV below E_F [8]. Nevertheless more recent magneto-optical spectroscopic investigations by Brändel *et al.* [9] can be viewed as an experimental confirmation of the calculated band structure of CrO_2 .

As mentioned above, the major application of CrO_2 is in magnetic recording [10]. Substitutions of Cr by Ir increase the coercive field by several orders of magnitude ($\cong 3\,000$ Oersteds) compared with that of the pure material for $\cong 5\% \text{Ir}$ [11-13]. For such low concentrations of Ir, larger coercivities were obtained after very high oxygen pressure treatments using KClO_3 as oxygen source in a belt type apparatus [14]. This remarkable increase arises from the *single-ion magneto-crystalline anisotropy* (MCA) i.e. from the spin-orbit coupling effects of Ir [15]. The latter was clearly identified as giving rise to MCA by a recent study of Coehoorn and Daalderop [16].

Here we examine the electronic and magnetic properties of substituted CrO_2 at different discrete concentrations by using the *augmented spherical wave* — ASW — method in its scalar relativistic implementation [17, 18]. Based on the local density approximation (LDA) [19], the ASW method uses the atomic sphere approximation (ASA) where the potential is assumed to be spherically symmetric within overlapping spheres centered at each atomic site. The total volume of the spheres should be equal to the cell volume. Hence in open structures such as that of CrO_2 , the ASA requires the use of *empty spheres* (ES) i.e. pseudo atoms with zero atomic number so that too large an overlap is avoided between the actual atomic spheres. The major role of the ES is to represent the interstitial charge. We stress that the choice of the radii of the spheres is non-unique.

In order to investigate relativistic effects in more detail we included spin-orbit coupling in a further step. Comparisons with other 5d substitutional elements (Sect. 5) will be undertaken in a second set of calculations.

Fig. 1 — Unit cells of rutile : a) and trirutile : b) Dashed and black spheres : Cr ; open spheres : O, [23]. The $(-)\text{-C}_2$ axes in (a) are found in (b) too, hence the same symmetry operations for the two structural setups provided that all respective spheres are equivalent.

2. Crystal structure setups for discrete amounts of substitutions.

2.1 THE SIMPLE CELL OF CrO_2 . — CrO_2 crystallizes in the rutile structure. The simple tetragonal unit cell ($a = 4.421 \text{ \AA}$, $c/a = 0.6596$) encloses two formula units ; it is represented in figure 1a. For a detailed description of the atomic as well as ES sites in the cell, the reader is referred to our previous article [5] and the erratum.

The presence of two Cr atoms in the simple cell allows for the study of the 50 % substitutions i.e. CrIrO_4 . Due to the large amounts of computing time of the spin-orbit modified ASW programs, such a composition could constitute a first approach for Ir-substitutions.

It is however at concentrations of substitutional elements far lower than 50 % that the relevant properties of CrO_2 appear. Hence multiple-cell arrangements must be set up.

2.2 DOUBLE CELL. — Doubling the cell along c with $a' = a$ and $c'/a = 1.32$ yields the same interatomic distances as in the simple cell. However a lower symmetry is obtained since the body-center does not correspond to an atomic position as in the simple cell. The presence of 4 Cr atoms enables us to simulate substitutions of 25 % when one Cr is replaced by one Ir.

In the simple and double cells the oxygen environment of the substitutional element was treated differently from that of Cr. In the following the oxygen atoms will be labelled O_1 and O_2 for the substitutional element (Ir) and host Cr, respectively. Throughout the different calculations, the designation of the empty spheres (ES) was the same as in [5] i.e. ES_1 in the vicinity of oxygen and ES_2 in the vicinity of the spheres of metal atoms.

2.3 TRIPLE CELL. — In order to approach the lower concentrations of substitutional element, i.e. around 10 % for which the interesting properties of CrO_2 start to appear, a triple cell was considered. A composition of $\text{Cr}_{0.833}\text{Ir}_{0.167}\text{O}_2$ could hence be simulated. The cell of CrO_2 was tripled along the c axis with $a'' = a$ and $c''/a = 1.979$. The resulting trirutile cell as shown in figure 1b has again the full symmetry operations of the simple cell provided all Cr sites are equivalent.

For the double and triple cells the validity of the structural setups was checked by the calculation of the electronic and magnetic properties of the non-substituted compound. Calculations were done with the sphere radii and the lattice constant a used for the former calculation of the simple cell (Tab. IIa, Ref. [5]). Due to the large number of species the number of $\mathbf{k}$ points had to be limited in order to achieve convergence in a reasonable time.

3. Methodology of the calculations and presentation of the results.

3.1 METHODOLOGY. — The experimental variation of the lattice parameters of the $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$ solid solution studied by Maestro *et al.* [11] was considered and the lattice constants for $x = 0.5$ and $x = 0.25$ were used to derive the a and c parameters for the simple and double cells respectively. The lattice parameters of pure CrO_2 were used to derive those of the triple cell. As a matter of fact the variations of the experimentally observed values of the a and c lattice parameters of the CrO_2 - IrO_2 solid solution for compositions near 10 % Ir are very small [11]. Whereas the solid solution compositions are *disordered*, our substituted phases are *ordered* by construction. This could constitute a limitation to the results when comparisons will be attempted with experiment ; i.e. whenever the consequence of disorder is important (cf. Sect. 3.2).

Calculations were self-consistently converged to obtain the electronic and magnetic properties. In a further step the results (converged values of the spin-dependent potential), were used as a starting point for the ASW calculations introducing spin-orbit coupling. This

was done for the Ir-substituted material in the simple and double cell only. Due to the large number of atomic species (42) in the triple cell and to a prohibitively large amount of computing time, only scalar relativistic self-consistent ASW calculations could be done.

3.2 PRESENTATION OF THE RESULTS. — The results of this study will be presented in the following manner :

* In section 4, the local partial charges and magnetic moments for calculations done firstly without then with spin-orbit coupling will be presented in tables Ia, b and IIa, b for the Ir-substitutions within the simple and the double cells, respectively.

The results will be extensively discussed for the simple cell together with the densities of states (DOS). Only differences will be assessed for the double and triple cells.

Table I. — *Local partial charges for majority ($\uparrow$) and minority ($\downarrow$) spins and site-projected magnetic moments for CrIrO_4 . ML = multiplicity. $a = 8.4688$ a.u. ; $c/a = 0.6875$; 36 k points. r (Cr, Ir, O) = 2.18875 a.u. ; r (ES) = 1.66276 a.u. (u.a. = atomic unit. 1 a.u. = 0.529 Å). a) Calculation converged before spin-orbit coupling. b) Spin-orbit coupling calculations using converged files of Ia.*

a	ML	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	Q_{Tot}	M_{at}
Ir	1	0.139	0.139	0.143	0.142	2.690	3.010	0.038	0.038	6.339	- 0.317
Cr	1	0.109	0.099	0.161	0.154	2.800	0.719	0.034	0.034	4.110	2.102
O ₁	2	0.899	0.900	2.280	2.320	0.059	0.052	—	—	6.510	- 0.035
O ₂	2	0.899	0.900	2.250	2.320	0.051	0.037	—	—	6.457	- 0.058
ES ₁	4	0.074	0.074	0.067	0.067	—	—	—	—	0.282	- 0.001
ES ₂	4	0.100	0.098	0.089	0.086	—	—	—	—	0.373	0.005

39.0 1 617 μ_B

b	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	μ_s	μ_l	M_{at}
Ir	0.140	0.139	0.146	0.145	2.710	2.960	0.038	0.037	- 0.247	- 0.060	- 0.307
Cr	0.109	0.099	0.162	0.154	2.810	0.709	0.034	0.034	2.114	- 0.064	2.051
O ₂	0.899	0.900	2.280	2.320	0.059	0.052	—	—	- 0.030	- 0.018	- 0.048
O ₁	0.899	0.900	2.250	2.310	0.051	0.037	—	—	- 0.047	- 0.008	- 0.055
ES ₁	0.072	0.072	0.067	0.067	—	—	—	—	- 0.001	- 0.001	- 0.002
ES ₂	0.106	0.103	0.089	0.086	—	—	—	—	0.005	0.001	0.006

Table II. — *Local partial charges for majority ($\uparrow$) and minority ($\downarrow$) spins and site-projected magnetic moments for Cr_3IrO_8 . ML = multiplicity. $a = 8.4348$ a.u. ; $c/a = 1.3469$; 36 k points. r (Cr, Ir, O) = 2.16501 a.u. ; r (ES) = 1.64464 a.u. a) Calculation converged before spin-orbit coupling. b) Spin-orbit coupling calculations using converged files of Ia.*

a	ML	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	Q_{Tot}	M_{at}
Ir	1	0.138	0.135	0.145	0.143	2.500	3.130	0.038	0.038	6.267	-0.621
Cr	3	0.110	0.099	0.164	0.156	2.750	0.707	0.035	0.035	4.056	2.056
O ₁	2	0.896	0.898	2.250	2.310	0.049	0.038	—	—	6.441	-0.059
O ₂	6	0.896	0.898	2.230	2.310	0.045	0.028	—	—	6.407	-0.068
ES ₁	8	0.074	0.074	0.064	0.065	—	—	—	—	0.277	-0.001
ES ₂	8	0.105	0.102	0.088	0.084	—	—	—	—	0.379	0.007

75.0   5.068 μ_B

b	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	μ_s	μ_l	M_{at}
Ir	0.140	0.136	0.148	0.146	2.580	3.040	0.038	0.038	-0.454	-0.083	-0.537
Cr	0.110	0.010	0.165	0.156	2.760	0.706	0.035	0.035	2.071	-0.108	-1.963
O ₁	0.896	0.898	2.250	2.310	0.049	0.037	—	—	-0.047	-0.009	-0.056
O ₂	0.897	0.898	2.240	2.310	0.045	0.028	—	—	-0.061	-0.009	-0.070
ES ₁	0.069	0.069	0.064	0.065	—	—	—	—	-0.001	-0.000	-0.001
ES ₂	0.102	0.099	0.088	0.084	—	—	—	—	0.007	0.0001	0.007

** In section 5, the effects on the band structure of CrO_2 within a double cell of different types of substitutional elements neighboring Ir, namely Os and Pt, will be studied.

4. Ir-substituted CrO_2 .

4.1 50 % SUBSTITUTION : CrIrO_4 . — Since the simple cell of CrO_2 comprises two formula units, the CrIrO_4 composition was obtained with one Cr replaced by one Ir. Tables Ia, b give the partial charges for majority ($\uparrow$) and minority ($\downarrow$) spins as well as the magnetic moments for CrIrO_4 without and with spin-orbit coupling respectively.

4.1.1 Charge distribution and magnetic moments. — As expected, charge transfer occurs from Ir and Cr spheres to those of O₁ and O₂. ES behave in the same way as in pure CrO_2 . charge transfer into ES₁ arises from oxygen atoms and charge transfer into ES₂ is from

metal spheres. Despite the equal volumes of the two types of ES the charge within ES_1 is lower. This is due to a « back-transfer » in the direction $ES_1 \rightarrow 0$ (charge accumulation) whereas for ES_2 transfer occurs only in the direction metal $\rightarrow ES_2$.

An antiparallel spin alignment between Ir and Cr is observed with a resulting total magnetization of $1.62 \mu_B$ (Bohr magnetons) per unit cell, lower than half of the value of magnetization of the pure material, i.e. $4 \mu_B$ or $2 \mu_B/\text{f.u.}$ (formula unit). This is obviously due to the loss of $2 \mu_B$ per one CrO_2 f.u. replaced by one non-magnetic IrO_2 f.u., on one hand, and to the antiparallel spin alignment of Ir, on the other hand (cf. Sect. 4.4). Moreover the magnetization is no longer an integer due to the loss of the gap at E_F of the minority spin states (cf. DOS section).

The magnitude of the moment of Cr ($2.10 \mu_B$) is slightly higher than in pure CrO_2 ($2.05 \mu_B$) due to 0.05 electron excess in the majority spin d sub-band. This behavior will be addressed in Section 4.4. The moments carried by the oxygen atoms in the vicinity of Ir (O_1) and Cr (O_2) are induced by a polarization of the p and d orbitals arising from the moments of the transition metals. The higher the magnitude of the latter, the larger the induced moment on oxygen.

Table Ib shows the results of the spin-orbit coupling calculation of CrIrO_4 . The orbital moment is in the same direction as the spin moment for Ir and of opposite direction for Cr. The explanation is straightforward if one considers Hund's rule i.e. the filling of the d shell for the two atoms ($> 5 \bar{e}$ for Ir i.e. more than a half-filled d-shell and $< 5 \bar{e}$ for Cr i.e. less than half-filled d-shell). It is interesting to note that although the orbital moment is nearly the same for both metallic atoms ($\approx -0.060 \mu_B$), its ratio to the spin-only moment is -3% for Cr and 24% for Ir. It should be noted that orbital contribution to the moment of Cr in pure CrO_2 was calculated to be -5% ($\mu(L)/\mu(S) = -0.11/2.02$) with a resulting moment of $1.92 \mu_B$. This contribution of ≈ 8 times for Ir is in agreement with the high spin-orbit constant known to characterize the 5d elements and especially Ir, whereas Cr (3d) which is expected to have a quenched orbital moment (spin-only element) exhibits a small orbital contribution to the total moment. The large difference between Ir and Cr is also obvious from the spin-orbit coupling of the d-band. The calculated spin orbit constants ζ are 0.027 and 0.004 Ry (2 944 and 452 cm^{-1}) for Ir and Cr respectively. Our self consistently calculated $\zeta(\text{Ir})$ value is close to the experimental value of tetravalent iridium: 3 000 cm^{-1} [20] and to that used by Mattheiss: $\zeta(d) = 0.033 \text{ Ry}$ ($= 3 620 \text{ cm}^{-1}$) in the first spin orbit calculations of 4d and 5d rutile oxides [21]. Total magnetization ($1.55 \mu_B$) is, as expected, lower than the value calculated without spin-orbit coupling but should be considered as being more reliable within such calculations.

4.1.2 Densities of states (DOS).

4.1.2.1 Partial DOS. — Figures 2a, b, c, d, e and f show the spin and site-projected DOS in units of states/eV at Ir, Cr, O_1 , O_2 , ES_1 and ES_2 sites respectively. The energy is counted with respect to E_F . At increasing energies — from left to right — the DOS are attributed to s, p and d states of oxygen and metal atoms. The DOS at the right hand panel of figure 3 (i.e. b, d and f) exhibit similarities to those of the pure system (Ref. [5], Fig. 5). This is what one expects from substitutions whereby the perturbation of the pure material remains rather *local* i.e. around the site of Ir. The Ir and Cr DOS show that the overlap between their d-states is mostly in the majority spin states as the Cr-d($\downarrow$)-DOS lie above E_F . A comparison of the d-DOS between $\uparrow$ and $\downarrow$ spins illustrates the magnitude of the magnetic moment which is essentially due to d-intraband polarization for a d element by a nearly rigid shift (Stoner) of the respective DOS: those of Ir are very little shifted and lie below E_F with a higher occupation of the d($\downarrow$) and hence the value of the moment is low and negative whereas those of Cr are more extensively shifted ($\uparrow$ below, and $\downarrow$ empty, above E_F) and the moment is much higher.

Turning now to the oxygen DOS, the $\text{O}(2p)$ -DOS exhibit a splitting, already apparent in figures 2a and b, into two parts that may be assigned to bonding states at lower energy and to anti-bonding or non-bonding for the higher energy parts respectively. The bonding character

Fig. 2. — CrIrO_4 : site and spin projected densities of states.

can be seen to be less significant in figure 2d (O_2) than in figure 2c (O_1). This tends to show different bonding behaviors of the two metal sublattices towards oxygen. The higher intensity of the 2p-bonding states observed for Ir is probably due to a more covalent Ir-O bond hence to a

Fig. 3. — CrIrO_4 : total spin projected densities of states. a) Scalar relativistic calculations. b) Scalar relativistic calculations with spin-orbit coupling.

stronger mixing. However care should be taken when interpreting these results since the overlap of the atomic spheres within the ASA is a function of the choice of their radii. From this standpoint it is difficult to address the ionic-covalent character of the chemical bond in CrO_2 .

Empty spheres show DOS (Figs. 2e and f) which exhibit mainly s and p character and show similarities with oxygen DOS as to the splitting and the shape. The main contribution to these spheres arises from oxygen for ES_1 (Fig. 2e) and metal atoms for ES_2 (Fig. 2f).

4.1.2.2 Total DOS and spin-orbit coupling effects. — Figures 3a and b show total DOS in both spin directions for the CrIrO_4 system obtained from calculations converged without and with spin-orbit coupling respectively. They present similarities as to their shapes and both have very close values of the density of states at E_F : 41.7 and 42.5 respectively. There are however some differences between them especially around E_F i.e. the d-DOS. From figure 3a ($\uparrow$) the first sharp peak below E_F belongs to Cr and is observed in the DOS of figure 2b. It arises from a band near E_F attributed in [5] to one localized spin of Cr *embedded* in a narrow band containing the other spin and crossed by E_F within the phenomenological scheme of the band structure of CrO_2 by Goodenough [22]. The second peak which is absent in figure 5a of reference [5], belongs to Ir-d($\uparrow$). For minority ($\downarrow$) spins, the peak observed in figures 3 is solely due to the Ir-d($\downarrow$). The main effect on the d-DOS of spin-orbit coupling can be seen in the splitting of the Ir-band at both spin directions i.e. lifting of degeneracy (Fig. 3a). Simultaneously there is a decrease in the intensity of the d-band peaks due to spin-orbit effects which affect not only Ir but Cr as well although spin-orbit coupling is small for a 3d element.

4.2 25 % SUBSTITUTION: Cr_3IrO_8 . — The double cell contains 4 formula units of CrO_2 thus allowing for 25 % substitutions i.e. Cr_3IrO_8 whereby one Cr is replaced by one Ir. Tables IIa, b give the partial charges for majority ($\uparrow$) and minority ($\downarrow$) spins as well as the magnetic moments without and with spin-orbit coupling respectively.

The same trends as in table Ia are observed for the charge transfers between the different spheres. It appears however that the system is more « ionic » as less electrons can be found in the Cr and Ir spheres. Oxygen spheres O_1 and O_2 are populated proportionally to their vicinity to Ir and Cr respectively and there is less back transfer in the direction $\text{ES}_1 \rightarrow 0$ whereas ES_2 population increases due to metal $\rightarrow \text{ES}_2$ charge transfer.

The antiparallel spin alignment is observed here too with a higher magnitude of the Ir moment: $-0.621 \mu_B$. This results from a depopulation of Ir-d($\uparrow$) states in favor of Ir-d($\downarrow$) ones. The higher polarization of the Ir-5d is an induced effect from neighboring Cr which are in a higher ratio to Ir than in CrIrO_4 . The moment of Cr is slightly lower than in CrIrO_4 and the resulting magnetization of the cell is $5.068 \mu_B$ for 4 formula units i.e. $2.534 \mu_B$ for two formula units, higher than in CrIrO_4 ($1.617 \mu_B$). This is, as expected, due to the lower ratio of Ir/Cr atoms (cf. Sect. 4.4). Here too the value of the magnetization is not an integer due to the disappearance of the gap. As a matter of fact the DOS presented in figures 4 (total : a), Ir : b), and Cr : c) for $\uparrow$ and $\downarrow$ show similar features to those of figures 2 but the intensity of the Ir-d($\downarrow$) peak is slightly higher and sharper so that E_F at 9.47 eV, is at the top of the Ir-d band. Just like CrIrO_4 , Cr_3IrO_8 is a *metallic ferrimagnet*.

Table IIb gives the results of the spin-orbit coupling calculation of Cr_3IrO_8 . The orbital moment at the site of Ir is higher than that calculated in table IIb but its ratio to the spin-only moment is 18 %, i.e. lower than in CrIrO_4 . Just like in the latter compound it adds negatively to the spin-only moment with a resulting total moment lower than in table IIa. The spin moment of Cr is higher than in table IIa but the orbital contribution is larger than that calculated for Cr in CrIrO_4 with a ratio of -5% and the resulting moment is $1.963 \mu_B$.

Fig. 4.

Fig. 4. — Cr_3IrO_8 : a) total DOS, b) Ir-DOS, c) Cr-DOS.

Fig. 5.

Fig. 5. — $\text{Cr}_5\text{IrO}_{12}$: a) total DOS, b) Ir-DOS, c) Cr-DOS.

4.3 16.7 % SUBSTITUTION: $\text{Cr}_5\text{IrO}_{12}$. — The triple cell contains 6 formula units of CrO_2 and the $\text{Cr}_{1.833}\text{Ir}_{0.167}\text{O}_2$ composition is simulated in an ordered manner within the « Cr_6O_{12} » compound where one Cr is replaced by one Ir. The oxygen spheres are not inequivalent in these calculations due to the large cell and no spin-orbit coupling calculations could be carried out.

Table III. — *Local partial charges for majority ($\uparrow$) and minority ($\downarrow$) spins and site-projected magnetic moments for $\text{Cr}_5\text{IrO}_{12}$. ML = multiplicity. $a = 8.3545$ a.u. ; $c/a = 1.9787$; 36 k points. r (Cr, Ir, O) = 2.12963 a.u. ; r (ES) = 1.61772 a.u.*

	ML	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	Q_{Tot}	$M_{\text{at.}}$
Ir	1	0.134	0.131	0.147	0.145	2.440	3.090	0.041	0.040	6.168	− 0.641
Cr	5	0.107	0.097	0.167	0.159	2.680	0.685	0.037	0.037	3.969	2.013
O	12	0.891	0.893	2.250	2.310	0.044	0.026	—	—	6.414	− 0.042
ES ₁	12	0.074	0.073	0.064	0.064	—	—	—	—	0.275	0.001
ES ₂	12	0.109	0.106	0.092	0.087	—	—	—	—	0.394	0.007
										111.0	9.009 μ_B

The same trends in tables I and IIa as concerning the charge transfers between the different spheres are observed here. For table III the tendency to a more « ionic » system is even more pronounced as the number of electrons in Ir and Cr spheres is decreased and charge transfer into empty spheres is higher for ES₂ and lower for ES₁.

The slightly larger magnitude of the magnetic moment of Ir (− 0.64 μ_B) as with respect to its value in Cr_3IrO_8 (− 0.62 μ_B) points to a *saturation* of the Ir intra-band polarization. The depopulation of the Ir-d($\uparrow$) states in favor of Ir-d($\downarrow$) states is more pronounced. There is a decrease of the moment of Cr with respect to its value in Cr_3IrO_8 and the resulting magnetization of the cell is $\approx 3 \mu_B$ for two formula units, higher than in Cr_3IrO_8 due to the lower ratio of Ir/Cr atoms. The value of the magnetization is very close to an integer due to the disappearance of the gap. The DOS given in figures 5 (total, Ir and Cr for $\uparrow$ and $\downarrow$; and Ir at corner position) show similar features to those of figures 4 but the intensity of the Ir-d($\downarrow$) peak is slightly higher and sharper so that E_F is at the top of the Ir-d band making the system a metallic ferrimagnet.

4.4 DISCUSSION OF THE Ir-SUBSTITUTED CrO_2 . — Along the series CrO_2 , $\text{Cr}_5\text{IrO}_{12}$, Cr_3IrO_8 and CrIrO_4 , the magnetization per f.u. strongly decreases (2.0, 1.50, 1.27 and 0.81 μ_B respectively, spin-only moments). This variation compares reasonably well, although not in absolute values of magnetization, with experimental data on the $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$ solid solution ($0 < x < 0.3$) [11, 13] which are systematically lower in magnitude. For $x = 0, 0.05, 0.1, 0.2$ and 0.3 the experimentally derived values at zero magnetic field [11, 13] are $\approx 1.3, \approx 0.4, \approx 0.25, \approx 0.09$ and $\approx 0.05 \mu_B$ respectively. The difference in magnitude

between the calculated and experimental magnetizations for the pure material could arise from particle size effect whereby very small submicron sized particles present in the sample could behave as superparamagnetic ones. As a matter of fact it is shown in [13] that substitution with Ir leads to an increase of the particle size. The difference in magnitude between the calculated and experimental values of the magnetization for the Ir substituted CrO_2 could be addressed on the basis of structural order (calculations) *versus* disorder (experimental). When the structure is ordered, a substitutional Ir is surrounded by a shell of nearest neighbor host Cr atoms which incur its direct influence (hybridization, magnetic couplings, ...) whereas the other shells of Cr atoms at larger distances undergo a decreasing influence from Ir. This should explain the strong decrease of the calculated magnetizations when the ratio Ir/Cr increases. However in the actually disordered $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$ system every Cr_{1-x} « sees » one Ir_i and undergoes its effect leading to the experimentally observed magnetization. Furthermore our calculations have only been made for the bulk. Surface effects (unusual oxidation states of Ir, spin canting, etc.) are ignored. These effects could be significant for powder samples having sub-micronic particle sizes in decreasing the magnetization. The decrease of Curie temperature T_c within the same composition range [11] is an indication of a decrease of ferromagnetic couplings. In the system under consideration here the latter subside in favor of antiferromagnetic couplings as the amount of Ir increases. This is shown by the antiparallel spin-alignment between Cr and Ir in our calculations.

From our results it appears that the basic mechanism underlying the spin alignments and the magnitude of the moments is the hybridization between Cr and Ir d-states. From tables Ia, IIa and III, the following observations can be made :

* The increase of the magnetic moment of Ir when the amount of Cr increases is an indication that it is an induced one, brought about by neighboring Cr band polarization through the mixing between their respective orbitals.

** The moment of Cr decreases as the hybridization effect between 1 Cr and 1 Ir is smaller when the amount of the latter is smaller. This points to the lower 5d character within the 3d band as one proceeds back towards the pure (non-substituted) material.

The increase of the charge in Cr sphere and its decrease in that of Ir when the amount of the latter decreases would be an indication of a *charge transfer material*. However the effect of charge transfer is not the predominant feature when the metal $\rightarrow$ oxygen electron transfers are compared between the different amounts of substitutional Ir. This reflects a rather localized picture of the magnetic moments.

For the 16.7 % Ir system it is interesting to note that the presence of E_F on top of the Ir-d band — contrary to CrIrO_4 or Cr_3IrO_8 — makes the system halfway between a metal and half metallic ferrimagnet. This is obviously a function of the dopant concentration whereby for low concentrations (say $x_{\text{Ir}} \leq 0.1$) CrO_2 should remain a *half metallic ferromagnet* just like the pure material. But for higher concentrations the electrical conductivity should be higher as the system becomes totally metallic with a larger DOS at E_F when the amount of Ir increases. This is in agreement with the experimentally observed enhancement of the conductivity when x_{Ir} increases [11].

5. Effect of the nature of the M substitutional on the band structure of CrO_2 .

5.1 MOTIVATION AND ASW RESULTS. — The results presented above show that the presence of iridium in the lattice of CrO_2 greatly affects its band structure. This is mainly shown by a transition from a half-metallic ferromagnet to a metallic ferrimagnet. In order to determine

whether it is an effect of the nature of the substitutional element we have performed two more calculations with two neighboring elements ($Z_{\text{Ir}} - 1$ and $Z_{\text{Ir}} + 1$), namely Os and Pt. For reasons of computational capacities we have selected the Cr_4O_8 structural set up where one Cr is replaced by Os or Pt. The results are given in tables IVa and c for the local partial charges at the two spin directions. For the sake of comparison within the 5d series, table IIa again is added as table IVb.

Table IV. — *Local partial charges for majority ($\uparrow$) and minority ($\downarrow$) spins and site-projected magnetic moments for Cr_3MO_8 , M = Os, Ir, Pt. $a = 8.4348$ a.u. ; $c/a = 1.34692$; 36 k points. r (Cr, M, O) = 2.16501 a.u. ; r (ES) = 1.64464 a.u. ML = multiplicity. a) M = Os. b) M = Ir. c) M = Pt.*

a	ML	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	Q_{Tot}	M_{at}
Os	1	0.128	0.125	0.140	0.138	2.040	2.450	0.041	0.040	5.102	− 0.399
Cr	3	0.108	0.098	0.162	0.154	2.800	0.669	0.035	0.035	4.061	2.150
O ₁	2	0.897	0.898	2.270	2.310	0.047	0.034	—	—	6.456	− 0.020
O ₂	6	0.897	0.898	2.250	2.300	0.044	0.026	—	—	6.415	− 0.037
ES ₁	8	0.075	0.075	0.065	0.065	—	—	—	—	0.280	0.001
ES ₂	8	0.107	0.104	0.089	0.084	—	—	—	—	0.384	0.008

$$E_{\text{MADELUNG}} = - 9.25 \text{ Ryd.}$$

$$\frac{73.999}{74.000} \quad 5.85 \mu_{\text{B}}$$

b	ML	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	Q_{Tot}	M_{at}
Ir	1	0.138	0.135	0.145	0.143	2.500	3.130	0.038	0.038	6.267	− 0.621
Cr	3	0.110	0.099	0.164	0.156	2.750	0.707	0.035	0.035	4.054	2.056
O ₁	2	0.896	0.898	2.250	2.310	0.049	0.038	—	—	6.441	− 0.059
O ₂	6	0.896	0.898	2.230	2.310	0.045	0.028	—	—	6.407	− 0.068
ES ₁	8	0.074	0.074	0.064	0.065	—	—	—	—	0.277	− 0.001
ES ₂	8	0.105	0.102	0.088	0.084	—	—	—	—	0.379	0.007

$$E_{\text{MADELUNG}} = - 8.86 \text{ Ryd.}$$

$$\frac{75.004}{75.000} \quad 5.068 \mu_{\text{B}}$$

Table IV (*continued*)

c	ML	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	$n_f^\uparrow$	$n_f^\downarrow$	Q_{Tot}	$M_{\text{at.}}$
Pt	1	0.155	0.149	0.155	0.150	3.290	3.350	0.037	0.037	7.323	- 0.048
Cr	3	0.110	0.099	0.165	0.156	2.750	0.691	0.035	0.035	4.041	2.081
O ₁	2	0.896	0.897	2.270	2.290	0.054	0.037	—	—	6.444	- 0.010
O ₂	6	0.896	0.898	2.240	2.300	0.047	0.027	—	—	6.408	- 0.040
ES ₁	8	0.074	0.073	0.065	0.065	—	—	—	—	0.277	0.001
ES ₂	8	0.103	0.100	0.088	0.083	—	—	—	—	0.374	0.007

$$E_{\text{MADELUNG}} = - 8.73 \text{ Ryd.}$$

$$\frac{75.99}{76.00} \quad 6.000 \mu_B$$

As far as all three calculations were performed with the same lattice parameters and sphere radii, one can establish some trends within the series $M = \text{Os, Ir, Pt}$ in addition to addressing the results of Cr_3IrO_8 in former sections :

— the charge within the M sphere increases with respect to the total charge leading to the following formal oxidation states of M : $\text{Os}^{+2.9}$ — nearly trivalent —, $\text{Ir}^{+2.74}$ and $\text{Pt}^{+2.66}$ i.e. decrease of the ionisation, simultaneously the charge on Cr increases from + 1.94 to + 1.96. The overwhole effect is a decrease of Madelung energy i.e. ionicity decreases.

— The magnetic moment of M increases from Os to Ir but vanishes for Pt. Total magnetization decreases from Os to Ir but increases again for Pt and becomes an integer value with $3 \mu_B$ per cell ($Z = 2$).

The total DOS at the two spin directions are shown for Os, Ir and Pt in figures 6a, b and c respectively. It is interesting to note that the evolution from upper to lower panels is governed by the energetic position of 5d band of M . The minority spin 5d band of Os lies on the Fermi level so that the material is perfectly metallic whereas that of Pt is far below E_F leading to a half metallic system. The Ir compound is obviously half way between the two extreme situations. There is a gap between oxygen 2p and the d (Cr, M) states which decreases in the series and disappears completely for the Pt system. This is consistent with the decrease of the Madelung energy so that the Os compound can be considered as more ionic and the Pt one less ionic than the Ir compound. Similar trends can be seen above E_F as to the disappearance of the gap.

5.2 DISCUSSION. — Adding one electron on M i.e. following the series $\text{Os} \rightarrow \text{Ir} \rightarrow \text{Pt}$ should lead to an increase of the mixing of the $M(5d)$ orbitals with those of neighboring atoms and to a broadening of the 3d band leading to a decrease of the Cr moment. This is indeed observed in the series from the DOS (Figs. 6a, b and c) and from the values of the magnetic moments in tables IVa, b and c. On the other hand, since the moment on M is induced by 3d polarization, it should decrease as the 3d moment. However from Os to Ir the contrary is observed. This should be a consequence of the mixing between the $M(5d)$ -Cr(3d) states whereby the

Fig. 6. — Cr_3MO_8 : densities of states a) $M = \text{Os}$, b) $M = \text{Ir}$, c) $M = \text{Pt}$.

mechanism of the increase of the 5d moment is the result of introducing a more pronounced 5d character for Ir than for Os into originally pure 3d states.

The size of the magnetic moment can be addressed with the help of the DOS (Fig. 6). Turning firstly to the majority spin DOS, from figures 6a and 6b there is a strong mixing between the host Cr-d and substitutional Os and Ir. This *smoothens* the effect of shifting the Fermi-level due to the different electron count *as if* Cr-d served as an additional reservoir. For this reason when going from Os to Ir the change of spin-up electrons is only 0.46. This is however much different for the minority-spin DOS, there we only have Os and Ir d-states at E_F and the difference in electron count is higher (0.78). The spin-down DOS are then much more shifted in energy. This explains the rapid increase of the magnetic moment from Os to Ir.

The vanishing magnetic moment of Pt can be explained by the position of the 5d band of Pt in figure 6c which lies below the 3d band of Cr. This involves the absence of any mixing between the two bands for both spin directions and the 5d band of Pt undergoes little intra-band polarization. An alternative interpretation can be found within the framework of crystal field effects. The electron occupation of Pt(5d) is close to 6. By assuming a nearly octahedral environment for the metal, the crystal field splitting of the d orbitals gives a low energy lying t_{2g} manifold and an e_g one at higher energy. The large energy separation between the two manifolds — crystal field splitting — is expectedly large for a 5d element so that the 6d-electrons are most likely to occupy the t_{2g} orbitals with an antiparallel spin arrangement — low spin — giving thus a zero magnetic moment.

If one now considers the total d-electron count there are roughly 6.5, 5.5 and 4.5 electrons for Pt, Ir and Os respectively i.e. a decrease of one electron along the series. The consequence is a less than filled t_{2g} orbital for the latter two elements, hence a finite magnetic moment carried by Ir and Os.

Dedication and acknowledgments.

This paper is dedicated to the memory of the late Professor E. P. Wohlfarth who untimely left us 5 years ago.

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