

## Orbital magnetism in Fe, Co, and Ni

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The spin and orbital contributions to the magnetic moments of Fe, Co, and Ni are calculated from first principles, using the linear muffin-tin orbitals method with the spin-orbit coupling treated at each variational step. In these calculations the spin and orbital moments agree with previously reported results obtained from spin-polarized Dirac calculations. When Hund's second rule is accounted for in the band Hamiltonian by adding an additional term for orbital polarization, the orbital moments agree better with experiment and the trends in the experimental orbital moments across the series can be explained. Specifically, the maximum orbital moment for Co is shown to occur because of its hcp equilibrium crystal structure.

### INTRODUCTION

The magnetic properties of Fe, Co, and Ni have previously been thoroughly investigated.<sup>1</sup> For instance, on the theoretical side, the magnetic moments have been calculated self-consistently from first principles, and good agreement with experiment has been found.<sup>2</sup> This theory used a band picture together with the local spin-density approximation (LSDA).<sup>3</sup> Thus, it is reasonable to assume that the band picture is essentially correct for Fe, Co, and Ni and hence they form an excellent testing ground for further theoretical refinements attempting to go beyond the LSDA, to remove the remaining small discrepancies between theory and experiment.

It is known that the LSDA fails in describing the  $\gamma$ - $\alpha$  transition in Ce.<sup>4,5</sup> This type of failure is typical when the LSDA is applied to narrow-band systems. However, by going beyond LSDA to treat all of Hund's rules in the band Hamiltonian, a good description of the  $\gamma$ - $\alpha$  transition in Ce was recently obtained in Ref. 5. Hund's first rule (maximum spin) was included by using the LSDA for the exchange splitting. By allowing for orbital polarization it was shown that an  $-E^3 L^2/2$  term in the total energy described Hund's second rule well (maximum orbital angular momentum).<sup>5</sup> Here  $E^3$  is the Racah parameter<sup>6</sup> of the  $f$  states (for  $d$  states the Racah parameter is denoted  $B$ , which we will use in the following) and  $L$  is the orbital moment of the system. This expression for the orbital polarization energy was obtained by a mean-field treatment<sup>5</sup> of the interaction<sup>7</sup>  $l_i \cdot l_j$  ( $l_i$  being the orbital moment of electron  $i$ ). This means that at the variational step and for each  $k$  point an orbital with azimuthal and magnetic quantum number  $(l, m_l)$  will be shifted an amount  $Bm_l L$ . Finally, Hund's third rule (for total angular momentum) was treated by including the spin-orbit coupling self-consistently at each variational step<sup>8</sup> (VS). The third Hund's rule can alternatively be accounted for by solving the spin-polarized Dirac (SD) equation,<sup>9</sup> and it is one of the goals of this paper to compare results treating Hund's first and third rule in the two different approaches

(VS and SD). We would also like to test the approach suggested in Ref. 5 for the orbital polarization of Fe, Co, and Ni. However, the main motivation for this work is to explain the published experimental results<sup>10</sup> on the orbital contribution to the magnetism in these systems and especially to understand why it peaks for Co. We will choose this sensitive quantity together with the spin moment to compare theory and experiment.

Magnetism in the  $3d$  metal alloys is known to follow the Slater-Pauling curve. This curve indicates that adding impurities with more unpaired spins than the host increases the magnetism (Fe in Co, for example). The spin moments of the  $3d$  elements themselves follow such a curve, which can be understood using band-filling arguments based upon spin pairing. To explain the spin moment in Fe, Co, and Ni it is important to first point out that the majority spin band is mostly filled in all these systems. Therefore, when going from Fe to Co and then Ni, which has the effect of adding more valence electrons, the minority spin band has to become more populated with these extra electrons and the spin moment drops accordingly. In the  $3d$  systems the orbital moment is expected to result from the spin-orbit interaction. Therefore, one might intuitively expect the orbital moment to correlate with the spin moment and possibly also to follow some kind of Slater-Pauling curve. However, experiments show that this is not the case, since the orbital moment in Co is much larger than in Fe and Ni. As we will see below, there are a number of factors that determine the size of the orbital moment, but it is mainly because of the different crystal structure that the observed maximum occurs for Co.

In our calculations we have used the linear muffin-tin orbitals (LMTO) technique<sup>8</sup> for bcc Fe, fcc Fe, fcc Co, hcp Co, and fcc Ni at their experimental volumes [with Wigner-Seitz radii,  $R_S$ , of 2.662 (Fe), 2.621 (Co), and 2.602 (Ni) in a.u.] in the same way as described in Ref. 5, using 140 (bcc), 240 (fcc), and 180  $k$  points (hcp) in the irreducible part of the Brillouin zone. Furthermore, the von Barth-Hedin parametrization<sup>11</sup> of the LSDA was

used. At each iterational step the Racah parameter  $B$  was recalculated and thus the relativistic calculations were parameter free and self-consistent.

### RESULTS

The calculated spin and orbital moments are listed in Table I. Here we list the moments obtained from a spin-polarized calculation (VS) as well as the results obtained from a spin-and-orbital-polarized calculation. Both calculations also included spin-orbit coupling. In Table I we also list the results obtained from a spin-polarized Dirac calculation<sup>12</sup> as well as experimental data.<sup>10</sup> We first turn our attention to the calculations (VS) that included spin-polarization as well as the spin-orbit coupling in an  $(l,s)$  basis. Since time-reversal symmetry is now broken, an induced orbital moment is obtained. The size of both the spin and orbital moments are in good agreement with the results obtained from the spin-polarized Dirac calculation. Hence, it seems that treating the spin-orbit coupling at the variational step within an  $(l,s)$ -basis set representation yields results that are very close to those obtained from a spin-polarized Dirac calculation.

However, as seen in Table I, neither of the two approaches (VS and SD) give results in satisfactory agreement with experiment for the orbital moment. Similar poor results were found in earlier studies on the uranium mononictides<sup>13</sup> and the actinide-iron Laves phases.<sup>14</sup> In contrast, the orbitally polarized (OP) calculations on actinide<sup>13,14</sup> and rare-earth systems<sup>5</sup> as well as the present work have predicted orbital moments that resemble the experimental values quite well. The main difference from the earlier orbitally polarized calculations is that in Fe, Co, and Ni the orbital moment is very small and the total moment is dominated by the spin component. The small value of the orbital moment in  $3d$  systems is a consequence of the well-known crystal-field quenching of the orbital moment together with the fact that the spin-orbit coupling parameter is relatively small in these systems. This is why previous spin-polarization-only calculations (in LSDA) have been able to achieve relatively good agreement with experimental data for the net magnetic moment.

To develop an intuitive understanding of our results, it is useful to discuss them in terms of the Slater-Pauling

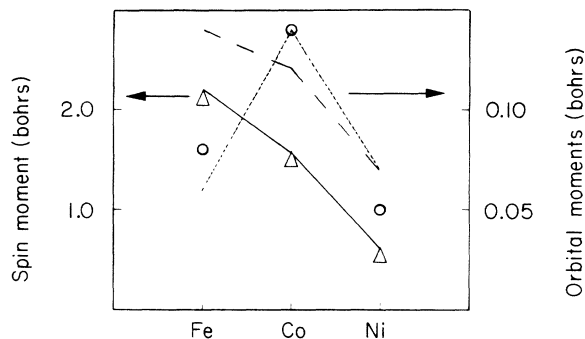


FIG. 1. Spin and orbital moments for Fe, Co, and Ni. The curves are straight lines connecting our theoretical values. The solid curves refers to the spin moment, the dotted curve to the orbital moment (in the experimental crystal structure) and the dash-dotted curve to the orbital moment in the hypothetical fcc phase of Fe and Co and the true fcc phase of Ni. The experimental spin moments are marked by triangles whereas the experimental orbital moments are marked by open circles.

curve. To illustrate this we show in Fig. 1 the calculated as well as the measured spin moments; the monotonic decrease in the spin moment is obvious. In Fig. 1 we also show the calculated and the experimental values of the orbital moments and it is seen that, with a maximum in the middle at Co, they do not correlate in any simple way with the spin moment. However, the crystal structures of Fe, Co, and Ni are all different and in order to eliminate variations in the orbital moment due to these differences we have also calculated the spin and orbital moments for Fe and Co in the fcc structure (Table I and Fig. 1). First, notice that for the fcc structures the orbital moments monotonically decrease just like the spin moment. Second, it is seen that the change in the true crystal structures (bcc in Fe and hcp in Co) lowers the orbital contribution in Fe and raises it in Co, so the experimental trend is obtained. Finally, note that adding the orbital polarization term gives the calculated values within  $0.02\mu_B$  of the experimental values in all cases.

The trends in the orbital moment for Fe, Co, and Ni in the fcc phase can now be understood as follows. When the spin-orbit coupling  $l \cdot s$ , is introduced in the band Hamiltonian, there will be matrix elements of the type  $l_z s_z$  (and

TABLE I. Spin and orbital moments for Fe, Co, and Ni.

	Fe (bcc)		Co (hcp)		Ni (fcc)	
	$\mu_{spin}$	$\mu_{orb}$	$\mu_{spin}$	$\mu_{orb}$	$\mu_{spin}$	$\mu_{orb}$
SD	2.12	0.04 <sup>a</sup>	1.54	0.07 <sup>a</sup>	0.57	0.05 <sup>a</sup>
	2.22	0.04 <sup>b</sup>	1.59	0.09 <sup>b</sup>	0.60	0.05 <sup>b</sup>
VS	2.22	0.04 <sup>c</sup>	1.57	0.09 <sup>c</sup>	0.61	0.05 <sup>c</sup>
	2.20	0.07(fcc) <sup>c</sup>	1.60	0.07(fcc) <sup>c</sup>		
OP <sup>d</sup>	2.21	0.06 <sup>e</sup>	1.57	0.14 <sup>e</sup>	0.61	0.07 <sup>e</sup>
	2.22	0.14(fcc) <sup>e</sup>	1.60	0.12(fcc) <sup>e</sup>		
Expt.	2.13	0.08 <sup>f</sup>	1.52	0.14 <sup>f</sup>	0.57	0.05 <sup>f</sup>

<sup>a</sup>Ebert *et al.*, Ref. 12.

<sup>b</sup>Gunbanov, Ref. 12.

<sup>c</sup>This work, no orbital splitting.

<sup>d</sup>Orbitally polarized calculations.

<sup>e</sup>This work, orbital splitting.

<sup>f</sup>Experiment Ref. 10.

$l_{+s} - l_{-s}$ ). Hence the spin-up electron states with positive (negative) magnetic quantum numbers ( $m_l$ ) will be pushed up (down). Exactly the opposite is found for spin-down electrons. Therefore, the contribution to the total orbital moment from the spin-up (down) electrons is negative (positive). Filled bands, of course, give no contribution. Fe, which has almost all of the spin-up states filled, will therefore have a positive orbital moment due to the partially filled spin-down bands. However, some of the spin-up states are unfilled because of hybridization with the very broad  $sp$  band, and we calculate a small negative contribution ( $\sim -0.03\mu_B$ ) from these states. Before continuing, it is worth noticing that the magnetic state in fcc-Fe is actually a meta magnetic one.<sup>15</sup> In Co and Ni the spin-down band becomes more completely filled. The positive orbital contribution from these states also drops (when completely filled, these bands give no contribution). This is slightly compensated, because in Co and Ni the spin-up band is also more completely filled and the tiny negative contribution to the orbital moment due to hybridization is, therefore, suppressed even more ( $\sim -0.02\mu_B$  for both systems). Hence Co will show an orbital moment similar to Fe. However, for Ni the spin-down  $d$ -band-filling effect dominates, and the orbital moment therefore drops.

To illustrate this we show in Fig. 2 a very simplified state density for Fe, Co, and Ni in their fcc phase. The correct number of valence electrons is here simply obtained by shifting the Fermi level to higher energies, as indicated in Fig. 2. As is also indicated in Fig. 2, the spin-up band in Fe is filled and we have a negligible orbital moment from this subband, leaving only a positive moment associated with the minority states. The same situation is found in Co, and from the schematic figure we would argue that the orbital moment should be very close to the one found in Fe, as is also the case (Table I and Fig. 1). However, in Ni the minority  $d$  band also starts to become completely filled and therefore there is a drop in the orbital moment as indicated in Fig. 2. Hence, the trend in the orbital moments in Fe, Co, and Ni, in the fcc phase, can also be viewed as following a Slater-Pauling type of curve, being heavily influenced by band-filling effects. However,

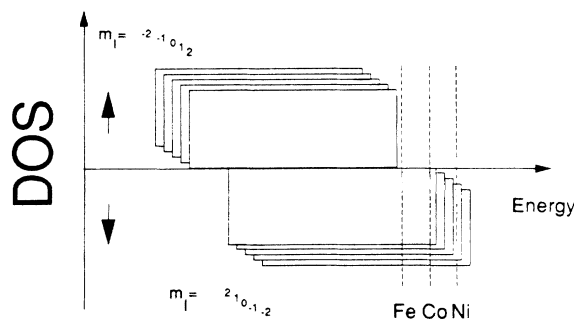


FIG. 2. Model state density for fcc Fe, Co, and Ni. Due to the spin-orbit coupling the degeneracy between the  $m_l$  and  $-m_l$  states is lifted and an orbital moment develops. The correct number of valence electrons is obtained by adjusting the Fermi level as marked in the figure (Fe, Co, and Ni).

the orbital moments in these systems in their true crystal structures are shown not to correlate in a simple way to the spin moments because of the different crystal structures.

The development of an orbital moment in the presently investigated systems is a parasitic effect, since it would be zero if the spin moment was also zero. The orbital moment results from the breaking of time-reversal symmetry when the system polarizes. The inclusion of the orbital-polarization term,  $-BL^2/2$ , merely enhances the already existing (from a VS calculation) orbital moment. To see this we proceed with an analysis analogous to what leads to the Stoner criterion for the onset of spin magnetism. Consider, for instance, a normal spin-polarized band. If the spin-orbit splitting is not included, states with spin  $\sigma$  and with magnetic quantum number,  $\pm m_l$  will be degenerate. We then ask the question, how much kinetic and potential energy is induced if we impose on the system an arbitrarily small splitting such that the difference between adjacent  $m_l$  states is  $H$ . The change in potential energy can be written

$$\Delta E_{\text{pot}} = -\frac{1}{2} H^2 B \left[ \sum_{m_l=-l}^{+l} (m_l)^2 D_{m_l} \right]^2. \quad (1)$$

Here  $H$  is the arbitrary small splitting which we eventually will let go to zero,  $m_l$  is the magnetic quantum number, and  $D_{m_l}$  is the value of the state density at  $E_F$  of the state  $m_l$ . The increase in kinetic energy can be written

$$\Delta E_{\text{kin}} = +\frac{1}{2} \sum_{m_l=-l}^{+l} H^2 (m_l)^2 D_{m_l}. \quad (2)$$

The criterion for the onset of orbital magnetism is now when the energy gain in Eq. (1) outweighs the loss in Eq. (2), i.e.,

$$BD_{\text{eff}} \geq 1, \quad (3)$$

where  $D_{\text{eff}}$  is

$$D_{\text{eff}} = \sum_{m_l=-l}^{+l} D_{m_l} (m_l)^2. \quad (4)$$

In very narrow-band systems Eq. (3) is fulfilled and an orbital moment can exist, although the spin-orbit splitting is omitted. However, in Fe, Co, and Ni,  $D_{\text{eff}}$  is of the order of 50 states/Ry and  $B$  is of the order of 10 mRy. Therefore, the ‘‘orbital Stoner product’’ is about 0.5 and the system remains in the symmetric nonpolarized state.

## CONCLUSIONS

To summarize, we have found that the treatment of the spin-orbit coupling within an  $(l,s)$  basis gives results comparable to those obtained from the spin-polarized Dirac equation. By analyzing the orbital contribution to the magnetic moment in the fcc structure for Fe, Co, and Ni we have shown that this contribution approximately scales

with the spin moment. However, the orbital moment is very sensitive to the crystal structure; using the correct crystal structure leads to a decrease of the orbital contribution in Fe (bcc) and an increase in Co (hcp) so that the experimental trend is obtained. Thus, including orbital polarization leads to orbital moment values in agreement

with experimental values. We believe that these calculations therefore give strong evidence that the experimental orbital values, which are difficult to obtain, are indeed correct and reasonable, despite the apparent lack of correlation with the spin moment caused by the different crystal structures.

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<sup>1</sup>For an overview see articles in *Ferromagnetic Materials*, edited by E. P. Wohlfarth and K. H. J. Buschow (Elsevier, Amsterdam, 1988).

<sup>2</sup>J. F. Janak and A. R. Williams, *Phys. Rev. B* **14**, 4199 (1976); V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978); O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollar, *Physica* **86-88B**, 249 (1977).

<sup>3</sup>P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1969); W. Kohn and L. J. Sham, *Phys. Rev. A* **140**, 1133 (1965).

<sup>4</sup>D. Glötzel, *J. Phys. F* **8**, L163 (1978).

<sup>5</sup>O. Eriksson, M. S. S. Brooks, and B. Johansson, *Phys. Rev. B* **41**, 7311 (1990).

<sup>6</sup>G. Racah, *Phys. Rev.* **62**, 438 (1942).

<sup>7</sup>J. H. Van Vleck, *Phys. Rev.* **45**, 405 (1934).

<sup>8</sup>O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975); H. L. Skiver, *The LMTO Method* (Springer, Berlin, 1984).

<sup>9</sup>P. Strange, F. Rosicky, and B. A. Ackermann, *Z. Phys. B* **52**,

31 (1983); G. Schadler, P. Weinberger, A. M. Boring, and R. C. Albers, *Phys. Rev. B* **34**, 713 (1986); H. Ebert, P. Strange, B. L. Gyoffry, *J. Phys. F* **18**, L135 (1988).

<sup>10</sup>M. B. Stearns, in *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology*, edited by H. P. J. Wijn (Springer-Verlag, Berlin, 1986), Group 3, Vol. 19, Pt. a; D. Bonnenberg, K. A. Hempel, and H. P. J. Wijn, *ibid.*

<sup>11</sup>U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

<sup>12</sup>H. Ebert, P. Strange, and B. L. Gyoffry, *J. Phys. F* **18**, L135 (1988); L. Fritsche, J. Noffke, and H. Eckart, *ibid.* **17**, 943 (1987); B. C. H. Krutzen and F. Springelkamp, *J. Phys. Condens. Matter* **1**, 8369 (1989); V. A. Gubanov (private communication).

<sup>13</sup>M. S. S. Brooks, *Physica* **130B**, 6 (1985).

<sup>14</sup>O. Eriksson, M. S. S. Brooks, and B. Johansson, *Phys. Rev. B* **41**, 9087 (1990); O. Eriksson, B. Johansson, and M. S. S. Brooks, *J. Phys. Condens. Matter* **1**, 4005 (1989).

<sup>15</sup>V. L. Moruzzi, *Phys. Rev. Lett.* **57**, 2211 (1986).