

## Sign reversal of the orbital moment via ligand states

I. Galanakis,<sup>1</sup> P. M. Oppeneer,<sup>2</sup> P. Ravindran,<sup>3</sup> L. Nordström,<sup>4</sup> P. James,<sup>4</sup> M. Alouani,<sup>1</sup> H. Dreysse,<sup>1</sup> and O. Eriksson<sup>4,5</sup>

<sup>1</sup>*Institut de Physique et Chimie des Matériaux de Strasbourg, F-67037, Strasbourg, France*

<sup>2</sup>*Institute of Solid State and Materials Research, P.O. Box 270016, D-01171 Dresden, Germany*

<sup>3</sup>*Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway*

<sup>4</sup>*Department of Physics, Uppsala University, Box 530, S-75112 Uppsala, Sweden*

<sup>5</sup>*ABB Corporate Research, Västerås, Sweden*

(Received 1 December 2000; published 2 April 2001)

It is demonstrated that the coupling between spin and orbital moments in magnetic systems may—for certain materials—be reversed from antiparallel to parallel, via the influence of ligand states. This is exemplified by first-principles calculations for an intermetallic compound  $\text{VAu}_4$ , but the effect may be found also in other classes of materials. From a computational analysis of the influence of the ligand states, and from an expression based on perturbation theory, we show that ligand states, that traditionally are known only to quench the orbital moment, may produce anomalous orbital moments that violate Hund's third rule.

DOI: 10.1103/PhysRevB.63.172405

PACS number(s): 75.50.Cc, 71.20.Be, 71.55.Ak

The magnetic moment of a material, whether it is ferromagnetic, ferrimagnetic, or antiferromagnetic, is composed of a spin and an orbital moment. The coupling between these moments, parallel or antiparallel, is different for different materials and is dictated by the filling of the electronic shell. For systems with a less-than-half-filled shell the coupling is antiparallel and for systems with a more-than-half-filled shell the coupling is parallel. This finding is referred to as Hund's third rule and is explained to be due to the spin-orbit interaction.<sup>1</sup> Hund's rules were originally developed in atomic physics, where, e.g., the third rule refers to the coupling of the total angular momentum  $\mathbf{J}$  as  $\mathbf{J}=\mathbf{L}+\mathbf{S}$  for more than half filling of the electron shell and  $\mathbf{J}=\mathbf{L}-\mathbf{S}$  for less than half filling. In practice the effect of Hund's third rule may be observed from the absolute value of  $\mathbf{J}$  but it can also be observed from a calculation of the projection of the spin  $S_z$  and orbital angular momentum  $L_z$  using the theorem of Wigner and Eckart.<sup>2</sup> For systems with an electron occupation less than half filling  $S_z$  and  $L_z$  are hence antiparallel whereas for systems with more than half filling the coupling is parallel, as dictated by Hund's third rule. This observation becomes important for theories based on density functional theory as well as for many experiments, since often  $S_z$  and  $L_z$  are being calculated or measured. The effect of the spin-orbit coupling and hence Hund's third rule is present also in the solid state, even though crystal field and band formation effects may reduce the orbital moment to some extent. As yet the coupling of spin and orbital angular momentum has to our knowledge never been found to violate Hund's third rule in a magnetic solid.

For localized electron systems the spin and orbital moments are essentially given from atomic physics, with a complication sometimes emerging from the crystalline electric field that to some extent quenches the orbital moment. For materials with delocalized electron states the orbital moment is reduced compared to the corresponding atomic value. Examples of this are Fe, Co, and Ni, that have orbital moments of order  $0.05\text{--}0.15\mu_B$ .<sup>3</sup> However, as noted above the coupling between the spin and orbital moments has never been found to violate Hund's third rule,<sup>4,5</sup> simply because its mi-

croscopical origin, the spin-orbit coupling, is always present, whether the electron states are localized or delocalized, subject to a strong crystal field or not, or if they are eigenstates of an atom or of a solid.

Recently substantial experimental attention has been focused on the orbital magnetic moment, since although it is a small quantity in some of the pertinent materials it nevertheless has been argued to carry vital information about the magnetocrystalline anisotropy (MAE).<sup>6,7</sup> As a matter of fact, using perturbation theory, a relationship between the directional dependence of the orbital moment and the MAE has been derived,<sup>8,9</sup> which established the proportionality of the MAE and the directional dependence of the orbital moment. The proportionality relationship, although it has been argued not to always hold, must be considered as being important in establishing a microscopical understanding of the MAE of delocalized electron systems. A full understanding of the MAE has, however, not yet been achieved. Apart from the relationship to the orbital moment, two distinct contributions to the MAE were previously proposed: The lifting of degeneracies at the Fermi energy through the spin-orbit coupling,<sup>10</sup> and the effect of anisotropic ligand-field bonding.<sup>11</sup> Our present investigations emphasize the important role of the ligand field further, not only in the formation of the orbital moment, but even in driving the sign of the orbital moment.

The attempts to connect the orbital magnetic moment to other magnetic properties, such as the MAE, are also important with regard to current material research efforts to find avenues for improving on the magnetic properties of materials. In this paper we demonstrate, first, that the coupling between spin and orbital moments can actually be such that Hund's third rule is violated, and second, that by suitable choice of combinations of materials one can “tune” the coupling to be antiparallel or parallel irrespective of whether the electron shell is less or more than half filled. In addition we shall argue that the microscopical understanding of magnetism given here paves the way for the possibility to influence one, from an applications point of view, of the more central concepts of magnetism, i.e., the MAE, since this property determines the magnetic hardness which then may be uti-

lized in different applications. For instance, in many applications involving the conversion of mechanical energy to electric or vice versa, so-called soft magnetic materials (with a vanishingly small MAE) are desired since they reduce energy losses in these types of applications.

Although the results presented here will be argued to be of a general nature, and that thus the coupling between spin and orbital moments may not necessarily follow Hund's third rule, we will illustrate most of our findings with one example;  $\text{VAu}_4$ . This material has experimentally been found to be ferromagnetic with a Curie temperature  $T_C = 60$  K and the easy magnetization axis is along the crystallographic  $c$  axis.<sup>12–14</sup> Already the finding that two nonmagnetic elements that, when combined, give rise to magnetic order is cause of attention, but, as will be outlined, there are more important features displayed by the magnetism of this interesting material. The crystal structure is the  $\text{MoNi}_4$  type structure and is a body-centered tetragonal (bct) structure with five atoms in the primitive unit cell. Since  $\text{VAu}_4$  is peculiar in the sense that it is a ferromagnet that is constructed from nonmagnetic elements, attention has previously been paid to it, and theoretical first-principles calculations of the spin moments have been carried out before.<sup>15–17</sup>

The present first-principles calculations were made using both a full-potential linear muffin-tin orbital (LMTO) method<sup>18</sup> and the augmented-spherical-wave (ASW) method.<sup>19</sup> In our calculations we used the experimental lattice parameters for  $\text{VAu}_4$ , which are  $a = 6.382$  Å and  $c = 3.981$  Å. The calculations were based on the local spin-density approximation using the von Barth-Hedin parametrization.<sup>20</sup> In order to have well-converged basis functions in the LMTO calculations a so-called double basis set was employed, with two sets of  $4s$ ,  $4p$ , and  $3d$  orbitals for the V atom and two sets of  $6s$ ,  $6p$ , and  $5d$  orbitals for the Au atoms. The  $k$  space was sampled using the special  $k$ -point method and a small Gaussian of width 10 mRy was associated with the eigenvalues close to the Fermi level  $E_F$  in order to speed up convergence. The spin-orbit interaction was included at each variational step, a method that is known to reproduce results of the spin polarized Dirac equation with great accuracy.<sup>21</sup> The ASW calculations employed the spherical potential approximation, together with a single basis set, which consisted of the same orbitals for V, but for Au  $5f$  states were additionally included. The spin-orbit coupling was treated as in the LMTO calculations, and no Gaussian broadening was applied.

The calculated scalar relativistic electronic structure of  $\text{VAu}_4$  is shown in Fig. 1. In the figure one may note that the Au  $d$  band is rather wide and is mainly located between  $-8$  and  $-2$  eV. The V  $d$  band is substantially narrower and it exhibits a large exchange splitting. The V spin-up  $d$  states are located right at the Fermi level, whereas the spin-down  $d$  states are located above the Fermi level. As will be discussed below there is one more feature in the DOS that should be observed, namely, that there is rather strong hybridization between the Au  $d$  and V  $d$  states. This may best be seen for the Au  $d$  states that in the energy region where the V  $d$  states have their dominating weight, follow the features of the V  $d$  states, a traditional sign of hybridization. This is so, since

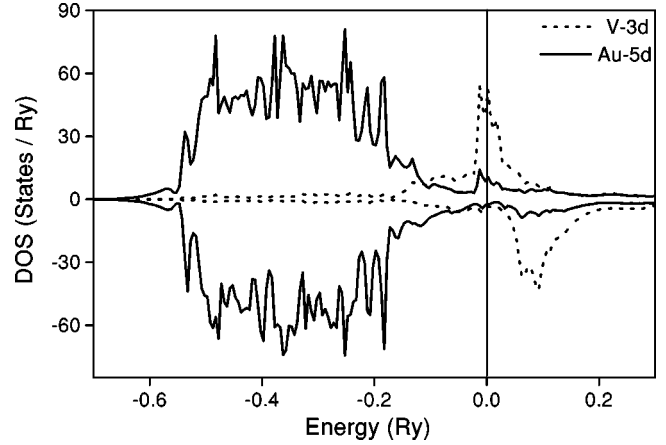


FIG. 1. Calculated density of states (DOS) for  $\text{VAu}_4$ . The DOS projected on the Au  $d$  orbitals are shown as full drawn lines and the DOS projected on the V  $d$  orbitals are shown as dotted lines. Spin up DOS are shown as positive and spin down as negative.

specific energy bands, that give rise to a particular feature in the DOS, have wave function character of basis functions located both on the V and Au atoms.

Let us now describe the most central finding of this study: the calculated spin and orbital moments of  $\text{VAu}_4$  (compiled in Table I). The calculated spin moment on the V atoms is with  $1.67\mu_B$  reasonably large. The previous computational study obtained a similar spin moment for V (Ref. 15) and both moments are larger than the experimental value of approximately  $1\mu_B$  at 4.2 K.<sup>14</sup> The orbital moment is  $0.16\mu_B$  (Ref. 22) and this represents at first sight a very anomalous result, since despite that V has a filling of the  $d$  shell that is less-than-half filled, the orbital moment is computed to be parallel to the spin moment. This represents, to our knowledge, the first prediction of a violation of Hund's third rule in a magnetically ordered material. Compared to the known orbital moments of  $3d$  elements in intermetallic compounds, the orbital moment is, in addition, remarkably large. Possible computational errors leading to the anomalous moment were ruled out by comparing the results of independent LMTO and ASW calculations, which indeed yielded nearly identical moments (see Table I and Ref. 23).

One may find a reason to this unusual coupling in a perturbation treatment. Recently, James *et al.*<sup>24</sup> elaborated on

TABLE I. Spin and orbital moments in  $\text{VAu}_4$ , as calculated with the FP-LMTO and ASW methods, both with and without (data indicated with an asterisk) the spin-orbit coupling on the Au atom. For comparison the moments calculated for V in  $\text{VCu}_4$  are also shown.

Compound	atom	method	spin ( $\mu_B$ )	orbital ( $\mu_B$ )
$\text{VAu}_4$	V	FP-LMTO	1.67	0.16
$\text{VAu}_4$	V	ASW	1.78	0.12
$\text{VAu}_4$	Au	FP-LMTO	0.003	-0.011
$\text{VAu}_4$	Au	ASW	0.003	-0.009
$\text{VAu}_4^*$	V	FP-LMTO	1.71	-0.10
$\text{VCu}_4$	V	FP-LMTO	2.08	-0.04

the work of Bruno,<sup>8</sup> and based on perturbation theory derived an equation for the orbital moment  $\mu_{\text{orb}}^{\tau}$  of, for instance, the magnetic V atom.<sup>24</sup> This was derived by expressing the nonrelativistic crystal wave function  $|\mathbf{k}i\rangle$  as

$$|\mathbf{k}i\rangle = \sum_{\tau m s} c_{\mathbf{k}i, \tau m s} |\tau m s\rangle, \quad (1)$$

where  $c$  is the basis-set expansion coefficient,  $|\tau m s\rangle$  a basis function, and  $\tau$ ,  $m$ , and  $s$  are the indices for the different atoms in the unit cell, the magnetic, and spin quantum number, respectively. The index  $i$  indicates a scalar-relativistic state and  $\mathbf{k}$  is a reciprocal-space vector. By inclusion of spin-orbit coupling in perturbation theory one can then derive<sup>24</sup> that

$$\mu_{\text{orb}}^{\tau} \propto \sum_{\mathbf{k}ij} \sum_{\tau' s} \sum_{m m' m'' m'''} n_{\mathbf{k}is, \tau m, \tau' m'} n_{\mathbf{k}js, \tau' m'', \tau m'''} \frac{\langle \tau m s | I_z | \tau m'' s \rangle \langle \tau' m' s | H_{so}^{\tau'} | \tau' m' s \rangle}{\varepsilon_{\mathbf{k}j} - \varepsilon_{\mathbf{k}i}}. \quad (2)$$

The quantity  $n_{\mathbf{k}is, \tau m, \tau' m'}$  is a product of wave-function characters of the scalar-relativistic states [from Eq. (1)], i.e.,  $n_{\mathbf{k}is, \tau m, \tau' m'} = c_{\mathbf{k}i \tau m s}^* c_{\mathbf{k}i \tau' m' s}$ . In this expression we observe that the orbital moment of atom  $\tau$  (V in our case) is influenced also by the spin-orbit parameter of the other atoms (ligand atoms) in the crystal, suggesting that the unusual magnetic properties of the V atom are influenced also by the spin-orbit coupling of the Au atoms. Since the Au spin-orbit coupling is substantially larger than that of V this contribution could be important. However, in order for the Au spin-orbit coupling matrix element to influence the V orbital moment, Eq. (2) indicates that there must be hybridization between the V and Au states, since otherwise  $n_{\mathbf{k}is, \tau m, \tau' m'}$  or  $n_{\mathbf{k}js, \tau' m'', \tau m''}$  is zero and the effect vanishes. The important consequence of Eq. (2) is that relativistic effects of the ligand atoms (Au) also influence the orbital moment of the V atom, and for the  $\text{VAu}_4$  this has extreme consequences. A version of Eq. (2) based on a Greens function formalism was presented in Ref. 25.

In order to elaborate on this further we performed additional calculations of the spin and orbital moments of  $\text{VAu}_4$ , turning off the spin-orbit interaction on the Au site, whereas keeping it for the V site. The so-calculated spin and orbital moments of the V atom are found to be in full accordance with Hunds third rule, with a V spin moment of  $1.71\mu_B$  and an orbital moment of  $-0.10\mu_B$ . Thus, the coupling is antiparallel as demanded by Hunds third rule. We also performed calculations for  $\text{VCu}_4$ , since the strength of the spin-orbit coupling of Cu is comparable to that of V and much

smaller than the one of Au. Also in this case Hunds third rule is obeyed and the spin and orbital moments are  $2.08\mu_B$  and  $-0.04\mu_B$ . This numerical exercise in combination with the discussion based on Eq. (2) demonstrates that the large spin-orbit coupling of the Au ligand atom influences, via hybridization, the orbital moment of the neighboring V atom to a surprisingly large extent, producing a parallel alignment of the spin and orbital moments.

An interesting scenario now emerges, since one by suitable tuning of Cu and Au concentrations may predict an alloy of  $\text{V}(\text{Au}_x\text{Cu}_{1-x})_4$  that may adopt a parallel or antiparallel coupling between spin and orbital moments, depending on concentration. One may even tune the concentration such that a vanishingly small orbital moment is found for the V atom. On account of the relationship between orbital moment anisotropy and MAE one may possibly influence the MAE such that an alloy with predicted zero MAE is identified. We note here that for this compound the proportionality relationship between the MAE and orbital moment anisotropy of Bruno<sup>8</sup> does hold, because the orbital moment is nonzero only for one spin channel, that of the majority spin (see also Ref. 9). From the total energy we have calculated the  $c$  axis to be the easy axis, which is also computed to be the axis having the largest orbital moment (the value of the MAE is  $1.78$  meV per unit cell and the orbital moment anisotropy is  $0.09\mu_B$ ). We have tested the possibility to reduce the MAE by alloying and performed calculations for the intermetallic compound  $\text{VAu}_2\text{Cu}_2$ . For this system the competition between the V and Au contributions to the orbital moment of the V atom are almost of equal size and hence nearly cancel each other. The net orbital moment is  $0.03\mu_B$  and the MAE is reduced to  $0.5$  meV per unit cell. A finer tuning of a low MAE has to involve noninteger concentrations of Au and Cu (or possibly Ag), and is outside the scope of the present paper.

To conclude, we have demonstrated that ligand states of a magnetic atom may influence the orbital magnetic moment in a way that is more complex than the simple ‘‘crystal field quenching.’’ The ligand states may actually induce large changes in the orbital moments that can lead to a violation of Hunds third rule. We have argued that hybridization between the ligand states and the magnetic ion is important for this effect to occur. The possibility to tune the orbital moment and MAE by suitable alloying has been proposed.

The support from TMR is acknowledged. O.E., L.N., and P.J. are grateful to NFR and TFR and the Swedish Foundation for Strategic Research (SSF) for support. We are grateful to Dr. J. M. Wills for providing the full potential code used in this work. Valuable discussions with Professor B. Johansson and Dr. L. M. Sandratskii are acknowledged.

<sup>1</sup>N. Ashcroft and D. Mermin, *Solid State Physics* (Holt-Saunders, Philadelphia, 1981).

<sup>2</sup>See e.g., A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1974).

<sup>3</sup>M.B. Stearns, in *3d, 4d, and 5d Elements, Alloys and Compounds*, edited by H.P.J. Wijn, Landolt-Börnstein, New Series, Group III, Vol. 19a (Springer, Berlin, 1986), p. 34.

<sup>4</sup>We note that an exception to Hunds third rule was found in a

- paramagnetic material U when an external magnetic field was applied (Ref. 5). The induced spin and orbital moment are both approximately  $2-3 \times 10^{-3} \mu_B$ . Here we discuss an entirely different situation, namely, the possible break down of Hund's third rule in a magnetically ordered material, having a spin moment of nearly  $2 \mu_B$ .
- <sup>5</sup>A. Hjelm, O. Eriksson, and B. Johansson, *Phys. Rev. Lett.* **71**, 1459 (1993).
  - <sup>6</sup>D. Weller, Y. Wu, J. Stöhr, M.G. Samant, B.D. Hermsmeier, and C. Chappert, *Phys. Rev. B* **49**, 12 888 (1994); D. Weller, J. Stöhr, R. Nakajima, A. Carl, M.G. Samant, C. Chappert, R. Mégy, P. Beauvillain, P. Veillet, and G.A. Held, *Phys. Rev. Lett.* **75**, 3752 (1995).
  - <sup>7</sup>N. Nakajima, T. Koide, T. Shidava, H. Miyauchi, H. Fukutani, A. Fujimori, K. Iio, T. Katayama, M. Nývlt, and Y. Suzuki, *Phys. Rev. Lett.* **81**, 5229 (1998).
  - <sup>8</sup>P. Bruno, *Phys. Rev. B* **39**, 865 (1989).
  - <sup>9</sup>G. van der Laan, *J. Phys.: Condens. Matter* **10**, 3239 (1998).
  - <sup>10</sup>G.H.O. Daalderop, P.J. Kelly, and M.F.H. Schuurmans, *Phys. Rev. B* **41**, 11 919 (1990); **50**, 9989 (1994).
  - <sup>11</sup>D.S. Wang, R. Wu, and A.J. Freeman, *Phys. Rev. B* **47**, 14 932 (1993).
  - <sup>12</sup>L. Creveling, H.L. Luo, and G.S. Knapp, *Phys. Rev. Lett.* **18**, 851 (1967).
  - <sup>13</sup>K. Adachi, M. Matsui, and Y. Fukuda, *J. Phys. Soc. Jpn.* **48**, 62 (1980).
  - <sup>14</sup>G. Kido, N. Miura, M. Matsui, and K. Adachi, *J. Magn. Magn. Mater.* **31-34**, 283 (1983).
  - <sup>15</sup>J. Kübler, *J. Magn. Magn. Mater.* **45**, 415 (1984).
  - <sup>16</sup>H. Yahagi, K. Yano, H. Itoga, A. Chaki, T. Ukai, and N. Mori, *J. Appl. Phys.* **69**, 4651 (1991).
  - <sup>17</sup>P.M. Oppeneer, I. Galanakis, P. James, O. Eriksson, and P. Ravindran, *J. Magn. Soc. Jpn.* **23**, S1,21 (1999).
  - <sup>18</sup>J. M. Wills (unpublished).
  - <sup>19</sup>A.R. Williams, J. Kübler, and C.D. Gelatt, *Phys. Rev. B* **19**, 6094 (1979).
  - <sup>20</sup>U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
  - <sup>21</sup>Compare, for instance, the orbital moments of the two methods in P. Söderlind *et al.*, *Phys. Rev. B* **45**, 12911 (1992); and P. Strange, H. Ebert, J.B. Staunton, and B.L. Györfy, *J. Phys.: Condens. Matter* **1**, 3947 (1989); P. Strange, J.B. Staunton, B.L. Györfy, and H. Ebert, *Physica B* **172**, 51 (1991).
  - <sup>22</sup>We investigated the sensitivity of the orbital moment with respect to choice of muffin-tin radius of the V atom and found that the calculated orbital moment does not depend strongly on this choice.
  - <sup>23</sup>The spin moment on V is somewhat smaller in the full-potential LMTO calculation, but one should not forget that in the latter scheme there is an additional interstitial spin moment of  $0.075 \mu_B$ . The calculated total moment per formula unit is  $1.87 \mu_B$  for the LMTO method and  $1.88 \mu_B$  for the ASW method.
  - <sup>24</sup>P. James, O. Eriksson, and L. Nordström (unpublished).
  - <sup>25</sup>I.V. Solovyev, P.H. Dederichs, and I. Mertig, *Phys. Rev. B* **52**, 13 419 (1995).