Calculations of the electronic spin and orbital magnetic moments and g' in ferromagnetic nickel

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The magnitudes of the electronic spin and orbital magnetic moments and the magnetomechanical ratio (g') for ferromagnetic nickel were calculated using the model-Hamiltonian approach of Ehrenreich and Hodges. Comparison of the calculated g' with the experimental value demonstrates the validity of the method. The good quantitative results for both the orbital moment and g' show that it is possible to take account of spin-orbit coupling and incomplete quenching of orbital angular momentum in a simple way. It is suggested that the neglect of the orbital contribution can lead to errors of as much as 10% in related band calculations and theoretical work.

I. INTRODUCTION

In an earlier calculation of g' in nickel, Fletcher[1] used only simple $3d$ orbital functions, but obtained (perhaps somewhat fortuitously) good agreement with the presently accepted experimental g' value. His calculation was based upon a theory originally developed by Brooks.[2] Fletcher's calculation used the nickel density of states he had calculated previously,[3] together with several simplifying assumptions adopted for computational tractability.

Despite considerable *experimental* work[4,5-8] in the intervening years to demonstrate *unmistakably* the presence of a small but non-negligible orbital contribution to the magnetic moment of iron, cobalt, nickel, and their binary alloys, the orbital moment seems to have been neglected in energy-band calculations and related theoretical work. The energy-band calculations of Connolly,[9] Wakoh,[10] Callaway,[11] and others, as well as the model-Hamiltonian work of Ehrenreich et al.[12] have proceeded on the premise that the total contribution to the magnetic moment is due to electronic spin, i.e., the sum of the unpaired electron spins. This, of course, is not true since, in fact, there is also a small additional contribution from the orbital electronic moment which should be added to all spin-moment contributions, thereby modifying the previous author's comparisons of theoretical and experimental total magnetic moments. In many cases, because of the approach adopted in the calculations, this additional magnetic moment contribution diminishes the agreement between theory and experiment.

II. CALCULATIONAL FORMALISM

The magnetomechanical ratio (g') of a material is defined as the ratio of its total magnetic moment to its total angular momentum.[4] g' can range from 2 for pure spin moment to 1 for pure orbital moment. However, for most materials its value is usually close to 2 because most of the electronic orbital angular momentum is quenched (i.e., vanishes). In pure iron, cobalt, and nickel, as well as their binary alloys, however, the experimentally determined value of g' [13,5-8] is appreciably less than 2. This experimental result is clear evidence that there remains an unquenched orbital angular-momentum contribution.

In quantum-mechanical terms the total magnetic moment along the z direction is given by the term $\langle L_z + 2S_z \rangle$ and the total angular momentum along z by the term $\langle L_z + S_z \rangle$, so that the value of g' [4] is determined by the ratio of the two matrix elements, or

$$g' = \langle L_z + 2S_z \rangle / \langle L_z + S_z \rangle . \tag{1}$$

In the absence of spin-orbit coupling, the expectation value of $\vec{L}_z$, the orbital angular momentum, is always zero, leading to a g' value of 2. Therefore, in the calculation of g', the spin-orbit coupling term must be included in order to obtain a value of g' different from 2.

It would be a formidable task indeed to calculate the value of g' from a first-principles energy-band calculation with both spin-polarization and spin-orbit terms included. However, the interpolation scheme of Ehrenreich and Hodges[12] (EH) seems ideally suited for the calculation of g' in ferromagnetic nickel.

The EH scheme starts from a set of basis functions which consist of five linear-combination-of-atomic-orbitals (LCAO)-type atomic orbitals to represent the $3d$ functions for nickel, plus an additional four orthogonalized plane wave (OPW) functions to represent the conduction bands. This combination of basis functions gives rise to an

18-by-18 secular equation, using a Hamiltonian of the form

$$H = H_{band} + H_{s.o.} + H_{corr} \ , \tag{2}$$

where H_{band} is the usual nonrelativistic Hamiltonian, $H_{s.o.}$ contains the spin-orbit coupling, and H_{corr} contains the correlation and exchange effects which give rise to a spin-polarized or ferromagnetic band structure. Each of the nine (5 LCAO + 4 OPW) functions appears twice in the secular equation, once each for up and down spin orientations.

The energy matrix elements are given in the "model-Hamiltonian" sense,[12] with a number of adjustable parameters, the magnitudes of which are chosen to fit either the results of first principles calculations or experiments. The energy bands are then determined at a large number of points within the Brillouin zone and the properties which involve k-space integrations are determined. A detailed description of the EH approach is available in the literature.[12] However, a few comments are in order.

The spin-orbit term is allowed to couple only the $3d$ functions, since these matrix elements are well known. Hence the OPW functions of up-and-down spins are only indirectly coupled through their hybridization with the $3d$ functions. Hence the Ehrenreich-Hodges model can be briefly described as the hybridization of OPW functions with spin-orbit-coupled $3d$ functions within a parametrized model-Hamiltonian formalism.

The presently described g' calculation uses the EH formalism unchanged. After setting up the secular equation and diagonalization to determine the eigenvector coefficients, it merely remains to compute the expectation values of L_z and S_z [as given in (1)]. The forms of the additional matrix elements of L_x, L_y, L_z, S_x, S_y, and S_z are given in the Appendix. These expressions can then be used for the calculation of the expectation values of L and S for the spin-orbit-coupled $3d$ bands hybridized with the OPW conduction bands. These expectation values are obtained quite simply by calculations of

$$\langle \psi | \theta | \psi \rangle = \sum_{i=1}^{18} \sum_{j=1}^{18} a_i^* \, a_j \, \langle \phi_i | \theta | \phi_j \rangle \ ,$$

where the a's are the eigenvector coefficients obtained previously, ψ is, of course, the wave function, the ϕ's are the basis functions, and θ is one of the L or S operators given in the Appendix.

III. RESULTS AND DISCUSSION

The value of g' in nickel was calculated by the foregoing method using as parameters the set b of Ehrenreich and Hodges.[12] This set of parameters was based on a fit of the EH model to the paramagnetic band structure calculation of Hanus,[14] modified to obtain better agreement with various experiments, especially the magneton number. We believe that this set may not be the optimum choice but it is the best available at this time.

The present calculation gives a value of $g' = 1.862$ for the magnetization along the $\langle 111 \rangle$ axis (which is the easy axis of magnetization in nickel). This g' value is derived from a calculated $\langle S_{111} \rangle$ value of 0.302 and an orbital contribution from $\langle L_{111} \rangle = 0.048$. The present calculation has also been repeated for the $\langle 100 \rangle$ axis, for which the g' results are almost identical. We find that in this latter case for $\langle 100 \rangle$, $g' = 1.858$, derived from values of $\langle S_z \rangle = 0.303$ and $\langle L_z \rangle = 0.050$. While the calculated g' values agree fairly well with the experimental value (1.837), they are significantly too large. One might reasonably ask whether there is some obvious explanation of this difference.

In searching for an explanation for the large theoretical values, it was concluded that the discrepancy is a result of an incorrect premise in the original derivation of the EH b parameters. The present calculated value ($\sim 0.05 \mu_B$) for the orbital moment, in fact, agrees very well with the measured value ($0.051 \mu_B$). The spin moment $2\langle S_z \rangle$, on the other hand, ($0.606 \mu_B$) is considerably higher than the $0.552 \mu_B$ derived from g' and total moment measurements.[4] In fact, $0.606 \mu_B$ is *exactly* the *total* measured magnetic moment for nickel. Of course, because the calculated spin moment is too large, the calculated g' value is correspondingly too large also.

As stated previously, the EH parameters were chosen to obtain the best fit with experimental data. As a result it was reasonable to use them unaltered in the present calculation in order to take advantage of the fact that they had already been optimized. However, the optimization performed by Ehrenreich and Hodges appears to assume the total magnetization for nickel arises entirely from a spin contribution, with zero-orbital moment. Experimentally (as stated earlier), this assumption has been shown to be invalid.[4,5-8] In the absence of other optimized sets of parameters it was necessary to use the present EH ones but clearly the calculated spin moment would always be too large.

In conclusion let us note that the present calculation yields a very accurate value of the orbital moment in ferromagnetic nickel, using the model potential approach of Ehrenreich and Hodges. The EH parameters, however, overestimate the spin moment by nearly 10%, thus leading to a slight overestimate of g'.

APPENDIX A. MATRIX ELEMENTS OF $\vec{L}$ AND $\vec{S}$

The only expressions not explicitly given by Ehrenreich and Hodges[12] are for the matrix elements of orbital and spin angular momentum, $\vec{L}$ and $\vec{S}$. To be consistent with the approximations of Ehrenreich and Hodges, we neglect all inter-atomic contributions to the matrix elements of $\vec{L}$ (i.e., between orbitals on different sites) and all conduction band contributions. We retain intra-atomic contributions, between d orbitals on the same atomic site. The orbital angular momentum matrix elements are thus non-vanishing only among d functions on the same site and of the same spins. They are given as follows, between orbitals ϕ_μ which are cubic-symmetry-adapted d functions

$$\langle \phi_\mu \,|\, L_z \,|\, \phi_{\mu'} \rangle = \begin{pmatrix} 0 & 0 & 0 & 2i & 0 \\ 0 & 0 & i & 0 & 0 \\ 0 & -i & 0 & 0 & 0 \\ -2i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad ,$$

$$\langle \phi_\mu \,|\, L_x \,|\, \phi_{\mu'} \rangle = \begin{pmatrix} 0 & 0 & -i & 0 & 0 \\ 0 & 0 & 0 & -i & -i\sqrt{3} \\ i & 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 & 0 \\ 0 & i\sqrt{3} & 0 & 0 & 0 \end{pmatrix}$$

$$\langle \phi_\mu \,|\, L_y \,|\, \phi_{\mu'} \rangle = \begin{pmatrix} 0 & i & 0 & 0 & 0 \\ -i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i & i\sqrt{3} \\ 0 & 0 & i & 0 & 0 \\ 0 & 0 & -i\sqrt{3} & 0 & 0 \end{pmatrix}$$

The spin matrix elements couple only like functions of opposite spin. For the axis of spin quantization along the direction θ, ϕ, these are

$$\langle \Phi | S_z | \Phi' \rangle = \frac{1}{2} \begin{pmatrix} \cos\theta & -\sin\theta \\ -\sin\theta & -\cos\theta \end{pmatrix} ,$$

$$\langle \Phi | S_x | \Phi' \rangle = \frac{1}{2} \begin{pmatrix} \sin\theta \sin\phi & \cos\theta \cos\phi + i \sin\phi \\ \cos\theta \cos\phi & -\sin\theta \cos\phi \\ -i \sin\phi & \end{pmatrix} ,$$

$$\langle \Phi | S_y | \Phi' \rangle = \frac{1}{2} \begin{pmatrix} \sin\theta \sin\phi & \cos\theta \sin\phi - i \cos\phi \\ \cos\theta \sin\phi & -\sin\theta \sin\phi \\ +i \cos\phi & \end{pmatrix} .$$

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