Revised Model for 5d Electrons in the Heavy Rare Earth Metals

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Abstract. A revised version of a recently published model for 5d electrons in the ferromagnetic state of the heavy rare earth metals is described. The model involves the broadening of local 5d states into overlapping bands with individual widths W. In the new approach it is assumed that the local 5d wave functions lie at some point between those for atomic 4f^n 5d^2 6s^2 configurations and those calculated for such configurations subject to the restriction that the 4f shell is kept with its moment rigidly fixed in some given direction. The admixture of non-aligned 4f states as in the atom lowers the local energy, but it also lowers the 5d bandwidth due to misfit of the 4f states which occur with and without the presence of a 5d electron. This second effect raises the energy of the low lying states in the band. The best local states are determined by minimising the total electronic energy of the system, using approximations which are most suitable for 4f shells with large excitation energies. Bandwidths are found by fitting the observed saturation magnetic moments in Gd and Tm, and satisfy W \approx 1 \text{ eV}.

In two recent papers [1, 2], the second of which will be referred to as I, an attempt was made to use published analyses [3-7] of 4f^n 5d^2 6s^2 configurations in the heavy rare earth atoms to form a basis for a study of 5d electrons in the corresponding metals. Each level \( \varepsilon \) of the atomic configuration can be associated with a particular 5d state to a fair approximation. The energies \( E_\varepsilon \) of these states were assumed to broaden into a set of overlapping bands in the solid, and the partial densities of states associated with individual 5d levels were taken to be uniformly spread over widths \( W \) centred on the atomic energy levels. Information given in the published analyses for atoms was used to estimate magnetic moments \( \mu_\varepsilon \) associated with each 5d state. Then, after allowance for a small moment \( \mu_s \) due to 6s electrons, the excesses of observed saturation magnetic moments \( \mu_1 \) per atom above the values \( \mu_\varepsilon \) for tripositive ions were fitted by a model in which \( W \) was treated as an adjustable parameter for each material. The equations used were

\[ \sum_x n_\alpha \mu_\alpha = \mu - \mu_1 - \mu_s, \]  

\[ \sum_x n_\alpha (E_F - E_\alpha)/W, \]  

where \( E_F \) denotes the Fermi energy; the sums in Eqs. (1) and (2) are over all partially occupied states \( \alpha \). It was found that \( W \) lay in the range \( W = (0.84 \pm 0.16) \text{ eV} \) for the five materials Gd, Tb, Dy, Er and Tm. Such widths are considerably smaller than those indicated by band structure calculations [8, 9]. A treatment of Ho was not given in I because not enough information was available in the published results of analysis of the atomic configuration [10].

As described in the preceding paragraph, the procedure adopted to determine bandwidths seems to have much to be said in its favour. It is a great advantage to be able to make use of empirical atomic data to avoid...
having to attempt to calculate the complex effects of the local $4f - 5d$ interactions. However, in order to facilitate calculations of magnetic hyperfine fields and electric field gradients at nuclei, greatly simplified approximations to the true atomic functions were used for the application of the theory to Gd, Er and Tm. For these materials, state vectors were assumed in which the $4f$ shell remained in its ground state with its angular momentum rigidly fixed in a given direction $z$, and the $5d$ state vector $|\xi\rangle$ was taken to be of the form

$$|\xi\rangle = \xi |m_\xi, +\rangle \pm (1 - x^2)^{1/2} |m_\xi + 1, -\rangle,$$

where $m_\xi$ and $(m_\xi + 1)$ denote components of orbital angular momentum along the $z$ axis, and plus or minus denotes spin parallel or antiparallel to this direction. The magnetic moment for $5d$ states of this type, which we call $\mu_{so}$, is given by

$$\mu_{so} = m_\xi + x^2.$$  

Although this was not made entirely clear in I, state vectors of the above type are only an approximation to the true atomic functions even if the $4f$ shell in the atom remains completely in a state with maximum value of the total $4f$ angular momentum $J_f$. The states used were eigenfunctions of the components $J_{fz}$ and $I_{dz}$ of $4f$ and $5d$ angular momenta in the $z$ direction, whereas the atomic states are eigenfunctions of $J$ and $J_z$, where $J$ is the total angular momentum.

For Gd, Er and Tm, simplified wave functions of the type discussed were used in conjunction with true atomic energy levels in I, and so there was some inconsistency involved for these metals. A more consistent approach to determine bandwidths was used in Tb and Dy in that magnetic moments, denoted in the present paper by $\mu_{A}$, were determined from the published wave functions by use of

$$\mu_{A} = g_2 J_s - \mu_i,$$

where $J_s$ and $g_2$ are the total angular momentum and calculated $g$ factor for the state $x$, and $\mu_i$ is the magnetic moment of the tripositive ion. However, the published wave functions in Tb and Dy were not in a form convenient for the calculation of magnetic hyperfine fields or electric field gradients at nuclei. Also, if this type of approach is tried for Gd, no solutions of Eqs. (1) to (3) can be obtained, and so the method has serious drawbacks. An alternative possibility would be to use both wave functions and energies calculated on the assumption of a rigidly fixed $4f$ shell. This approach gives results for bandwidths similar to those obtained before for Gd, but does not work well for the other heavy rare earths.

After analysis we can see that neither the use of wave functions based on a rigidly fixed $4f$ shell nor the use of true atomic states would be expected to be correct in the solid. This is because use of true atomic functions introduces a reduction factor in the overlap integrals which occur in a tight binding band structure calculation, due to misfit of the $4f$ states $|f_0\rangle$ which occur when no $5d$ electron is present on a given site with states $|f_{a1}\rangle$ occurring when the local atomic state $z$ is occupied. This misfit factor depends on the sum $Q_z$ of occupation probabilities $p_{oa}$ of states of the $4f$ shell with non-maximum angular momentum quantum number in the $z$ direction (the magnetization being along the negative $z$ axis). This effect lowers the bandwidth, and so effectively raises the energy of the low lying states in the band.

However, the local energy is decreased by allowing the $4f$ shell to adjust so as to include some non-aligned part as in the $4f^{n}5d^{6s^{2}}$ states of the atom. The amount of this decrease $\Delta E_{oa}$ can be determined from a calculation with a rigid $4f$ shell in comparison with known data on atomic energy levels. Thus we have two competing tendencies, the bandwidth effect and the local effect. In this paper we assume that in the solid a fraction $X_{oa}$ of the atomic admixture of non-aligned $4f$ state occurs, and we determine $X_{oa}$ by minimising the total electronic energy. However, in order to obtain results, we need to calculate the fraction $Q_{z}$ of non-aligned states in the atom. To do this we make approximations, the main one of these being to ignore states of the $4f$ shell with total angular momentum $J_f$ differing from its maximum value, as opposed to states with maximum $J_f$ but non-maximum $J_{fz}$. This neglect is expected to be a good approximation for Gd and Tm, but poor for Tb, for which material the first excited state of the $4f$ shell is only about 2000 cm$^{-1}$ above the ground state.

The method of treatment of the local state problem given in the present paper may appear to be only a slight refinement of that used in I, but it has several significant advantages, as listed here.

(i) It removes most of the inconsistency in the previous approach to Gd, Er and Tm.

(ii) It enables estimates to be made of the reductions below free ion values of the $4f$ contributions to saturation magnetic moments.

(iii) It provides an approximate method of estimating the differences between ion and metal hyperfine fields and electric field gradients at nuclei in Tb, Dy and Ho, although we shall see that further refinements of the theory may be required to obtain reliable calculations of hyperfine fields in Tb.

(iv) It provides a basis for a new interpretation of