2015

Correlations in rare-earth transition-metal permanent magnets

Ralph Skomski
University of Nebraska-Lincoln, rskomski2@unl.edu

Priyanka Manchanda
University of Nebraska-Lincoln, priyanka.manchanda@vanderbilt.edu

Arti Kashyap
IIT Mindi, akashyap@lnmiit.ac.in

Correlations in rare-earth transition-metal permanent magnets

R. Skomski,[1,a)] P. Manchanda,[1] and A. Kashyap[2]
[1]*Department of Physics and Astronomy and NCMN, University of Nebraska, Lincoln, Nebraska 68508, USA*
[2]*School of Basic Science, IIT Mandi, Mandi, Himachal Pradesh, India*

It is investigated how electron-electron correlations affect the intrinsic properties of rare-earth transition-metal magnets. Focusing on orbital moment and anisotropy, we perform model calculations for 3d-4f alloys and density-functional theory (DFT) calculations for $NdCo_5$. On an independent-electron level, the use of a single Slater determinant with broken spin symmetry introduces Hund's rule correlations, which govern the behavior of rare-earth ions and of alloys described by the local spin density approximation (LSDA) and $LSDA+U$ approximations to DFT. By contrast, rare-earth ions in intermetallics involve configuration interactions between two or more Slater determinants and lead to phenomena such as spin-charge distribution. Analyzing DFT as a Legendre transformation and using Bethe's crystal-field theory, we show that the corresponding density functionals are very different from familiar LSDA-type expressions and outline the effect of spin-charge separation on the magnetocrystalline anisotropy. © 2015 AIP Publishing LLC.
[http://dx.doi.org/10.1063/1.4917003]

I. INTRODUCTION

Surprisingly, little is known about the atomic origin of rare-earth anisotropy, despite the technological importance of rare-earth transition-metal permanents magnets and despite the extended research on these materials. Crystal-field (CF) theory[1] and its close cousin ligand-field theory[2] provide a sound semiquantitative description of rare-earth anisotropy in terms of Hund's rules ionic states,[3,4] including hybridization effects.[2] In a strict sense, CF parameterization is a first-principle approach, because the only input is the atomic positions of the atoms. However, in practice, the crystal-field parameters are often determined phenomenologically,[2,4] and such theories, with choices of parameters and methods, may be called "second-principle" theories.

Correlation effects have been a major obstacle to the development of a first-principle description of rare-earth anisotropy, but similar effects also occur in some 3d systems, such as CoO.[5] Present-day first-principle calculations are largely based on the independent-electron approximation, mapping the $1/|\mathbf{r} - \mathbf{r}'|$ Coulomb interaction between electrons onto a "mean field". Such calculations amount to the consideration of a single Slater determinant constructed from one-electron wave functions $\psi_\mu(\mathbf{r})$. This includes Hund's-rules correlations in rare-earth ions[6] as well as calculations based on the local spin density approximation (LSDA), including approaches such as $LSDA+U$ and selfinteraction corrections (SIC). These correlations arise by choosing a Slater determinants with broken spin symmetry,[6] as contrasted to "true" correlations.[2] Such calculations exist for a variety of rare-earth transition-metal intermetallics, such as Sm_2Fe_{17}, $Sm_2Fe_{17}N_3$,[7] and Sm_2Co_{17},[7] $NdCo_5$,[8,9] and $Pr_2Fe_{14}B$.[10]

Magnetic-anisotropy calculations require high accuracies, to account for subtle details such as the oscillatory dependence of the magnetic anisotropy as a function of the number of d electrons.[11,12] This affects not only the choice of computational methods and parameters, such as the number of k-points in independent-electron calculations, but also leads to the question to what extent the anisotropy is affected by correlations going beyond a single Slater determinant.

II. SCIENTIFIC BACKGROUND

Correlation effects are caused by the Coulomb interaction $1/4\pi\varepsilon_o|\mathbf{r} - \mathbf{r}'|$ between pairs of electrons located at $\mathbf{r}$ and $\mathbf{r}'$.[6,13,14] Subject to the Pauli principle, integration over $\mathbf{r}$ and $\mathbf{r}'$ yields a repulsive energy (U) if an extra electron is added to an orbital. A simple quantum-mechanical mean-field approach is to use a single independent-electron Slater determinant to evaluate the Coulomb interaction. Examples of this approach are Hund's-rules correlations,[2,6] LSDA and $LSDA+U$,[15] and SIC.[6] By contrast, methods such as configuration interactions (CI), dynamical mean-field theory (DMFT), and density-matrix renormalization group (DMRG) simultaneously involve two or more Slater determinants.[16]

Independent-electron approaches to correlations fairly well reproduce features such as the formation of magnetic moments and local electron counts (configurations),[6] but fail to address more complex phenomena, such as spin-charge separation in Kondo systems and the fractional quantum-Hall effect.[6,16,17] As we will show below, the magnetic anisotropy of localized ions is very similar to spin-charge separation.

Figure 1 illustrates the meaning of spin-charge separation for a magnet where localized (4f) spins are embedded in a gas of itinerant (3d) atoms. The independent-electron magnetism of the 3d electrons is well-described by LSDA,

---

a)Author to whom correspondence should be addressed. Electronic mail: rskomski@neb.rr.com.
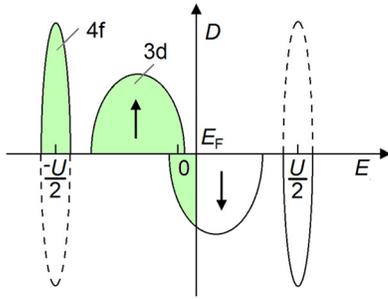
117, 17C740-1

FIG. 1. Schematic spin-polarized densities of states for a 3d-4f intermetallic. The difference between the solid and dashed lines reflects spin-charge separation.

whereas that of the 4f electrons requires improved potentials such as

$$V_i(\mathbf{r}) = V_{\mathrm{LSDA}}(\mathbf{r}) + U\left(\frac{1}{2} - n_i\right). \tag{1}$$

This equation, where n is the electron density and i labels the atoms, establishes the $\mathrm{LSDA} + U$ approximation.[18] However, strongly correlated (4f) moments are easy to switch by a small magnetic field (dashed line in Fig. 1). For one 3d electron interacting with one 4f electron, the problem can be solved exactly[4,6,14,19] and leads to the conclusion that the switching field is proportional to t^2/ε, where t is the 3d-4f hopping integral and ε is the orbital energy difference between the two states, the localized states lying lower. In the independent-electron approach, the corresponding expression is proportional to t.[6,16]

It is often assumed that correlations are of secondary importance in the ground state, because density-functional theory (DFT) is exact. However, this strategy requires the knowledge of the *exact* density functional. The interaction of a spin with an external magnetic field is a one-electron effect easily described by adding a Zeeman term to Eq. (1), meaning that the problem lies in the $\mathrm{LSDA} + U$ density functional. In fact, the model leading to the above t^2/ε splitting corresponds to a density functional proportional to $\sqrt{n}\sqrt{1-n}$,[14] which is very different from Eq. (1), including local-density terms such as $n^{1/3}$.

The purpose of DFT is to describe the ground state of electrons in an "external" crystal-field potential $V(\mathbf{r})$ created by atomic cores. Quantum-mechanically, many-electron systems involve a large number of wave functions $\psi(\mathbf{r}_1, \mathbf{r}_2,\ldots)$ and one generally needs to consider both ψ and ψ^*. The mapping of such complicated systems onto a single real density $n(\mathbf{r})$, which creates a "quantum mechanics without quantum mechanics," has the character of a Legendre transformation.[20] This transformation is very similar to the switching between variables T and S in the free energy $F = U - TS$, which is possible due to the bilinear coupling term TS. In the present case, the energy is

$$E = E_o(\psi_\mu, \psi_\mu^*, \ldots) - \Sigma_\mu \int \psi_\mu^*(\mathbf{r}) V(\mathbf{r}) \psi_\mu(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{2}$$

where E_o contains all interactions except the interaction with the external field and μ labels the many-electron quantum

states. Since $\Sigma_\mu\ \psi_\mu^*(\mathbf{r})\ \psi_\mu(\mathbf{r}) = n(\mathbf{r})$, the coupling term is indeed bilinear and we can write

$$E(n) = E_o(n) - \int n(\mathbf{r}) V(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{3}$$

From this equation, we obtain the ground-state energy by minimizing E with respect to $n(\mathbf{r})$. The individual wave functions $\psi_\mu, \psi_\mu^*, \ldots$ no longer appear in Eq. (3), but to properly realize the Legendre transformation, it is necessary to treat the full many-electron Hamiltonian. As emphasized by Lieb,[20] the connection between V and n is "extremely complicated and poorly understood." The challenge is not specifically quantum-mechanical but also occurs in classical Legendre transformations, as exemplified by the mechanical two-spring model of Fig. 2. (The exact solution and the corresponding Legendre transformation are given in the Appendix.)

The complex nature of DFT can be seen from Bethe's CF theory, which describes isolated magnetic ions of spin direction $\boldsymbol{\sigma}$, located at $\mathbf{R}$ and subjected to a crystal field $V(\mathbf{r}) = V_{\mathrm{CF}}(\mathbf{r})$. The corresponding density functional is

$$E(n(\mathbf{r}), \sigma) = -\Lambda \int \delta(n(\mathbf{r}) - n_{4f}(\sigma, \mathbf{r})) \mathrm{d}\mathbf{r} - \int n(\mathbf{r}) V(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{4}$$

where $\Lambda \to \infty$ enforces the 4f charge distribution $n_{4f}(\boldsymbol{\sigma}, \mathbf{r})$, which is rigidly coupled to the spin by spin-orbit coupling and described by the Stevens coefficients α_J, β_J, and γ_J.[3,4] As the $\sqrt{n}\sqrt{1-n}$ term above, the functional of Eq. (4) looks very different from the exchange-correlation potential normally assumed in DFT calculations.

III. LSDA + U AND ANISOTROPY

It is sometimes assumed[8] that $\mathrm{LSDA} + U$ accounts for strong 4f correlations and localization, including anisotropy. In fact, the 4f electrons do not become localized via Eq. (1) but retain Bloch periodicity, very similar to the decreased electron mobility in the tight-binding (TB) approximation, where the resistivity remains finite rather than undergoing a Mott transition.[21] Since anisotropy involves spin rotations, spin-charge separation is important.

A good example is the anisotropy of NdCo$_5$, based on both published work[8,9] and our own calculations. Uncorrected LSDA calculations, for example, using VASP code with a generalized gradient approximation (GGA), as described in Ref. 22, tend to cause numerical instability, because rare-earth 4f electrons are too far away from free-electron-inspired DFT, even if one adds gradient corrections. Stable moments are obtained by adding U for the Nd^{3+}, and varying U (and J) can be used to "fine-tune" the small
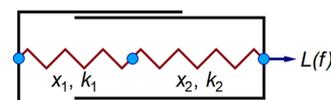

FIG. 2. Mechanical density-functional model, illustrating the removal of local degrees of freedom—x_i, or $\psi_i(\mathbf{r})$ and $\psi_i^*(\mathbf{r})$—in DFT-like Legendre transformations.

anisotropy energy, although these parameters are well-defined quantum-mechanically[18] and should not undergo second-principle adjustments.

A more fundamental problem is that LSDA + U yields a substantial orbital-moment anisotropy (OMA), which is contradictory to the experimental finding that Hund's rules are well satisfied in rare earths[2,23] and that the orbital moment shows little or no directional dependence,[24] in contrast to itinerant anisotropy.[25] This situation reflects the smallness of the crystal-field interaction (less than 10 meV) compared to the spin-orbit interaction (120 meV).[23] Taking the LSDA + U parameters $U = 7.0$ eV and $J = 0.97$ eV (Ref. 26) and performing the calculation for 504 k-points in the Brillouin zone, we obtain Nd orbital moments of $-3.65\,\mu_B$ in the a-b plane and $-4.53\,\mu_B$ along the c-direction, an OMA of 22%. Similar deviations from Hund's rules are obtained with full-potential (WIEN2k) calculations.[8,9]

IV. CORRELATIONS AND MAGNETIC ANISOTROPY

In the model considered above, the non-s character of the delocalized (3d) and localized (4f) electrons is not explicitly considered. To address this anisotropy-specific key feature, we consider the model of Figs. 3(b)–3(d) and use a matrix approach[19,21,27] that is physically equivalent to Refs. 6 and 14. We also take into account that the itinerant electrons have wave-function components that match the symmetry of the localized electrons.[28]

The model system contains a delocalized orbital (D) and two crystal-field variants of a localized d or f state with $L_z = 2$ (A, B), as shown in Figs. 3(c) and 3(d). There are altogether 9 product states, but 4 of them have two electrons in the localized orbitals, namely, Ψ_{AA}, Ψ_{AB}, Ψ_{BA}, and Ψ_{BB}. As explained elsewhere,[6,14,19] such product states have high correlations energies ($U \to \infty$) and can be ignored. Let us start with Figs. 3(c) and 3(d), where the spin is perpendicular to the paper plane. Arranging the remaining 5 states in the vector (Ψ_{AD}, Ψ_{BD}, Ψ_{DA}, Ψ_{DB}, Ψ_{DD}) yields the matrix Hamiltonian
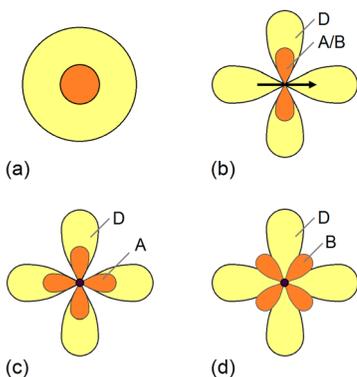

FIG. 3. Nontrivial correlations and anisotropy: (a) isotropic model, describing, for example, Kondo-like localized impurity states (brown) interacting with conduction electrons (yellow), (b) extension of the model to magnetic anisotropy, (c) and (d) localized orbitals that need to be considered in the simplest approximation.

$$H = \begin{pmatrix} A & i\lambda & 0 & 0 & t \\ -i\lambda & -A & 0 & 0 & 0 \\ 0 & 0 & A & i\lambda & t \\ 0 & 0 & -i\lambda & -A & 0 \\ t & 0 & t & 0 & \varepsilon \end{pmatrix}. \qquad (5)$$

Here, ε is the on-site energy of the localized electrons compared to that of the delocalized electrons,[6] λ is the spin orbit coupling, A is the crystal-field interaction, and t is the hopping integral between $|A\rangle$ and $|D\rangle$. (By symmetry, there is no hopping between $|B\rangle$ and $|D\rangle$.) For $A \ll \lambda \ll \varepsilon$, diagonalization of Eq. (5) yields the ground-state energy

$$E_c = -\lambda - A^2/2\lambda - t^2/2\varepsilon, \qquad (6)$$

where the index c means that the magnetization vector is parallel to the c-axis, or perpendicular to the paper plane in Figs. 3(c) and 3(d).

The Hamiltonian for the magnetization lying in the basal or a-b plane, as in Fig. 3(b), is similar to Eq. (2), but exhibits the following differences: (i) the hopping integral t is reduced to $t' \approx t/2$, because the lobes of Fig. 3(c) pointing to the left and right no longer contribute to the overlap responsible for hopping, (ii) the two localized orbitals of Figs. 3(c) and 3(d) are partially out of the plane of the delocalized electron, which gives rise to a common gain $A_o \approx A/2$ in repulsive crystal-field energy, and (iii) the energy splitting $\pm A$ is reduced to $\pm A'$, where $A' \approx A/2$, because the out-of-plane lobes do not contribute to the crystal-field splitting. This yields the in-plane energy

$$E_{ab} = -A_o - \lambda - A'^2/2\lambda - t'^2/2(\varepsilon + \lambda). \qquad (7)$$

The anisotropy energy per atom is $K = E_{ab} - E_c$, or explicitly

$$K = -A_o + A_{eff}^2/2\lambda + t_{eff}^2/2(\varepsilon + \lambda), \qquad (8)$$

where $A_{eff}^2 = A^2 - A'^2 \approx 3A^2/4$ and $t_{eff}^2 = t^2 - t'^2 \approx 3t^2/4$.

In Eq. (8), A_o is a Bethe-type crystal-field interaction term, $A_{eff}^2/2\lambda$ describes the effect of partial quenching, and $t_{eff}^2/2(\varepsilon + \lambda)$ is a correlation contribution reflecting spin-charge separation, similar to the well-established t^2/ε term in Sec. II, which would be of the order of t in the independent-electron approximation.

V. CONCLUSIONS

In summary, we have investigated correlation effects in rare-earth transition-metal intermetallics. On an independent-electron level, Hund's-rule correlations determine the behavior of 4f ions and of alloys described by LSDA and LSDA + U, the latter being a useful extension of the local-density approach. However, the behavior of rare-earth ions in a transition-metal host goes beyond independent-electron correlations. In particular, the dependence of the energy on the magnetization angle of the rare-earth spins involves spin-charge separation, which is poorly described by the independent electron approach. Our analysis outlines a novel approach towards orbital moment and anisotropy, providing the path towards a

deeper understanding of these phenomena and towards the search for new magnetic materials.

APPENDIX: LEGENDRE TRANSFORMATIONS AND LOCAL DEGREES OF FREEDOM

We consider an exactly solvable classical mechanical model, consisting of a series of two springs (Fig. 2). The energy of the system is

$$E = \frac{1}{2} k_1 x_1^2 + \frac{1}{2} k_2 x_2^2 - f L, \tag{A1}$$

where k_1 and k_2 are the two spring constants. The external force f is equivalent to the external potential $V(\mathbf{r})$ and the total length $L = x_1 + x_2$ is equivalent to the density $n(\mathbf{r})$. Minimizing E with respect to $x_{1/2}$ yields $x_{1/2} = f/k_{1/2}$ and $L = f(1/k_1 + 1/k_2)$, and substitution into Eq. (A1) yields $E = E_o(L) - f L$ with

$$E_o(L) = \frac{1}{2} \frac{L^2}{1/k_1 + 1/k_2}. \tag{A2}$$

This expression has the sought-for functional structure, because it depends on L only but not on f. This derivation shows that DFT is exact only if the underlying problem has been solved exactly, as contrasted to intuitive or limit-based approximations.

[1]H. Bethe, Ann. Phys. **3**, 133 (1929).
[2]C. J. Ballhausen, *Ligand Field Theory* (McGraw-Hill, New York, 1962).
[3]J. F. Herbst, Rev. Mod. Phys. **63**, 819 (1991).
[4]R. Skomski and J. M. D. Coey, *Permanent Magnetism* (Institute of Physics, Bristol, 1999).
[5]R. Skomski, X. Wei, and D. J. Sellmyer, J. Appl. Phys. **103**, 07C908 (2008).
[6]P. Fulde, *Electron Correlations in Molecules and Solids* (Springer, Berlin, 1991).
[7]L. Steinbeck, M. Richter, U. Nitzsche, and H. Eschrig, Phys. Rev. B **53**, 7111 (1996).
[8]H. Pang, L. Qiao, and F. S. Li, Phys. Status Solidi B **246**, 1345 (2009).
[9]G. J. Miletic and Ž. Blažina, J. Magn. Mater. **321**, 3888 (2009).
[10]J. Fidler *et al.*, IEEE Trans. Magn. (in press).
[11]M. T. Johnson, P. J. H. Bloemen, F. J. A. den Broeder, and J. J. de Vries, Rep. Prog. Phys. **59**, 1409 (1996).
[12]R. Skomski, A. Kashyap, A. Solanki, A. Enders, and D. J. Sellmyer, J. Appl. Phys. **107**, 09A735 (2010).
[13]L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).
[14]E. Runge and G. Zwicknagl, Ann. Phys. **5**, 333 (1996).
[15]V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
[16]*Strongly Correlated Systems: Theoretical Methods*, edited by A. Avella and F. Manchini (Springer, Berlin, 2012).
[17]A. J. Schofield, Contemp. Phys. **40**, 95 (1999).
[18]V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
[19]R. Skomski, J. Phys.: Condens. Matter **19**, 315202 (2007).
[20]E. H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).
[21]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).
[22]P. Manchanda, P. Kumar, A. Kashyap, M. J. Lucis, J. E. Shield, A. Mubarok, J. Goldstein, S. Constantinides, K. Barmak, L.-H. Lewis, D. J. Sellmyer, and R. Skomski, IEEE Trans. Magn. **49**, 5194 (2013).
[23]K. N. R. Taylor and M. I. Darby, *Physics of Rare Earth Solids* (Chapman and Hall, London, 1972).
[24]R. Skomski, A. Kashyap, and A. Enders, J. Appl. Phys. **109**, 07E143 (2011).
[25]P. Bruno, Phys. Rev. B **39**, 865 (1989).
[26]P. Larson and W. R. L. Lambrecht, Phys. Rev. B **75**, 045114 (2007).
[27]J. Zhang, R. Skomski, Y. F. Lu, and D. J. Sellmyer, Phys. Rev. B **75**, 214417 (2007).
[28]D. Schmitt, J. Phys. F **9**, 1745 (1979).