

# THE UNIVERSITY OF WARWICK

**Original citation:**

Petit, L., Paudyal, D., Mudryk, Y., Gschneidner, K. A., Pecharsky, V. K., Lüders, M., Szotek, Z., Banerjee, Rudra and Staunton, J. B.. (2015) Complex magnetism of lanthanide intermetallics and the role of their valence electrons : Ab Initio theory and experiment. Physical Review Letters, 115 (20). 207201 . ISSN 0031-9007

**Permanent WRAP url:**

<http://wrap.warwick.ac.uk/75646>

**Copyright and reuse:**

The Warwick Research Archive Portal (WRAP) makes this work of researchers of the University of Warwick available open access under the following conditions.

This article is made available under the Creative Commons Attribution- 3.0 Unported (CC BY 3.0) license and may be reused according to the conditions of the license. For more details see <http://creativecommons.org/licenses/by/3.0/>

**A note on versions:**

The version presented in WRAP is the published version, or, version of record, and may be cited as it appears here.

For more information, please contact the WRAP Team at: [publications@warwick.ac.uk](mailto:publications@warwick.ac.uk)

warwick**publications**wrap  
  
highlight your research

<http://wrap.warwick.ac.uk/>

## Complex Magnetism of Lanthanide Intermetallics and the Role of their Valence Electrons: *Ab Initio* Theory and Experiment

L. Petit,<sup>1</sup> D. Paudyal,<sup>2</sup> Y. Mudryk,<sup>2</sup> K. A. Gschneidner, Jr.,<sup>3</sup> V. K. Pecharsky,<sup>3</sup> M. Lüders,<sup>1</sup>  
Z. Szotek,<sup>1</sup> R. Banerjee,<sup>4</sup> and J. B. Staunton<sup>4,\*</sup>

<sup>1</sup>Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

<sup>2</sup>Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA

<sup>3</sup>Ames Laboratory, U.S. Department of Energy, and Department of Materials Science and Engineering,  
Iowa State University, Ames, Iowa 50011-3020, USA

<sup>4</sup>Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

(Received 14 April 2015; published 9 November 2015)

We explain a profound complexity of magnetic interactions of some technologically relevant gadolinium intermetallics using an *ab initio* electronic structure theory which includes disordered local moments and strong *f*-electron correlations. The theory correctly finds GdZn and GdCd to be simple ferromagnets and predicts a remarkably large increase of Curie temperature with a pressure of  $+1.5 \text{ K kbar}^{-1}$  for GdCd confirmed by our experimental measurements of  $+1.6 \text{ K kbar}^{-1}$ . Moreover, we find the origin of a ferromagnetic-antiferromagnetic competition in GdMg manifested by noncollinear, canted magnetic order at low temperatures. Replacing 35% of the Mg atoms with Zn removes this transition, in excellent agreement with long-standing experimental data.

DOI: 10.1103/PhysRevLett.115.207201

PACS numbers: 75.30.Kz, 71.20.Eh, 75.10.Lp, 75.50.Ee

Lanthanide compounds play an increasingly important role in the development of novel materials for high-tech applications which range from mobile phones and radiation detectors to air conditioning and renewable energies. Much of this stems from their magnetic properties, so that they are indispensable components in permanent magnets [1], magneto-responsive devices for solid state cooling [2], and other applications. Common to all the lanthanide elements is their valence electronic structure, which makes them chemically similar and also causes magnetic order. Lanthanide atoms are predominantly divalent ( $5d^06s^2$  valence electron configuration), becoming mostly trivalent in a solid, donating three valence electrons to the electron glue in which the atomically localized *f*-electron magnetic moments sit. The interaction between these moments derives from how the electron glue is spin-polarized. The Ruderman-Kittel-Kasuya-Yosida (RKKY) [3] free-electron model of this electronic structure is typically used to try to explain the many features of the indirect coupling of the *4f*-electron moments despite its rather poor representation of the *5d* states. The possible importance of the latter has already been inferred from some earlier electronic structure studies [4–7].

While theoretical aspects of lanthanide magnetism are well understood at the phenomenological level [8], predictive first-principles calculations are challenging owing to the complexities of the strongly correlated *f* electrons and itinerant

valence electrons along with the magnetic fluctuations generated at finite temperatures. In this Letter, we explore lanthanide compounds with an *ab initio* theory based on spin density functional theory (SDFT) in which the self-interaction corrected (SIC) local spin density (LSD) method [9,10] provides an adequate description of *f*-electron correlations [11–13] and the disordered local moment (DLM) theory [14] handles the magnetic fluctuations. We are able to give a quantitatively accurate description of the diverse magnetism of Cs-Cl (B2) ordered phases of Gd with Zn, Cd, and Mg which we test against experimental data and show the complex role played by the spin-polarized valence electrons.

Local moments of fixed magnitudes are assumed to persist to high temperatures and in lanthanide compounds are formed naturally from partially occupied localized *4f*-electron states. The orientations of these moments fluctuate slowly compared to the dynamics of the valence electron glue surrounding them. By labeling these transverse modes by local spin polarization axes fixed to each lanthanide atom *i*,  $\hat{\mathbf{e}}_i$ , and using a generalization of SDFT [14](+SIC [15,16]) for prescribed orientational arrangements,  $\{\hat{\mathbf{e}}_i\}$ , we can determine the *ab initio* energy for each configuration,  $\Omega\{\hat{\mathbf{e}}_i\}$  [16–19,24], so that the configuration's probability at a temperature *T* can be found. The magnetic state of the system is set by an average over all such configurations, appropriately weighted, and specifies the magnetic order parameters,  $\{\mathbf{m}_i = \langle \hat{\mathbf{e}}_i \rangle\}$ , where the magnitudes  $m_i = |\mathbf{m}_i|$  range from 0 for the high-temperature paramagnetic (PM) (fully disordered) state to 1 when the magnetic order is complete at  $T = 0 \text{ K}$ . A distribution where the order parameters are the same on every site,  $\{\mathbf{m}_i = m_f \hat{\mathbf{z}}\}$ , say, describes a ferromagnetically ordered

Published by the American Physical Society under the terms of the Creative Commons Attribution 3.0 License. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

(FM) state, whereas one where the  $\mathbf{m}_i$  alternate layer by layer between  $m_a\hat{x}$  and  $-m_a\hat{x}$  characterizes an antiferromagnetic (AF1) order. The free energy function  $\mathcal{F}(\{\mathbf{m}_i\})$ , written in terms of these magnetic order parameters  $\mathbf{m}_i$ , monitors magnetic phase transitions. It contains the effects of the spin-polarized valence electronic structure which adapts to the type and extent of magnetic order [19,25,26]. For lanthanide materials, the DLM theory describes how valence electrons mediate the interactions between the  $f$ -electron moments. These can turn out to be RKKY-like but can also show strong deviations from this picture as we find here for simple Gd-containing prototypes.

We start with GdZn, of particular interest in solid state cooling [27] but also because we expect its electronic structure to be straightforward [6,28]. The Gd atoms occupy a simple cubic lattice of the CsCl(B2) ordered phase. Our first-principles SIC-LSD calculations find the ground state Gd-ion configuration to be trivalent ( $\text{Gd}^{3+}$ ), with seven localized  $f$  states constituting a stable half-filled shell, in line with Hund's rules [11,12,19]. So Gd of all the heavy lanthanides has the relative simplicity of an  $S$  state for its  $f$  electrons, largely uncomplicated by crystal field effects and spin-orbit coupling. This permits a clinical look at how the interactions between large  $4f$ -magnetic moments are mediated by the valence electrons. These come from both the lanthanide and the post-transition metal Zn which has a low-lying, nominally filled,  $3d$  band added to its two  $s$  electrons. Our *ab initio* DLM theory can thus investigate the effect of the lanthanide  $5d$  electrons hybridizing weakly with  $3d$  states. This touches on a very important aspect of many magnetic materials containing both rare earth and transition metal elements [29], where understanding the interplay between the localized lanthanide magnetic moments and the more itinerant magnetism originating from the transition metal  $d$  electrons is paramount for the design of more efficient materials.

Our DLM theory calculations for the paramagnetic state of GdZn produce local moments of magnitude  $\mu \approx 7.3\mu_B$  on the Gd sites pointing in random directions so that there is no long-range magnetic order,  $\{\mathbf{m}_i = 0\}$ . The calculated paramagnetic susceptibility [16,17,19]  $\chi(\mathbf{q})$ , with a maximum at wave vector  $\mathbf{q}_{\text{max}} = (0, 0, 0)$ , shows that, in accord with experiment, GdZn develops FM order below a Curie temperature  $T_c = 184$  K (at theoretically determined lattice constant,  $a = a_{\text{th}} = 6.62$  a.u.), somewhat lower than the experimental value of  $T_c = 270$  K [30,31] (at  $a = a_{\text{exp}} = 6.81$  a.u.). We find that GdZn's  $T_c$  gradually decreases under pressure  $P$ , with calculated  $(dT_c/dP) = -0.45$  K kbar $^{-1}$ , which agrees qualitatively with the experimental value of  $-0.13$  K kbar $^{-1}$  from the literature [30] [Fig. 1(a)]. The negative  $dT_c/dP$  is typical of many metallic magnets owing to pressure-induced band broadening and diminished energy benefit from spin polarizing the valence electrons around the Fermi energy.

Naïvely, one might expect similar effects if Zn is replaced with isoelectronic Cd whose filled  $4d$ -band states

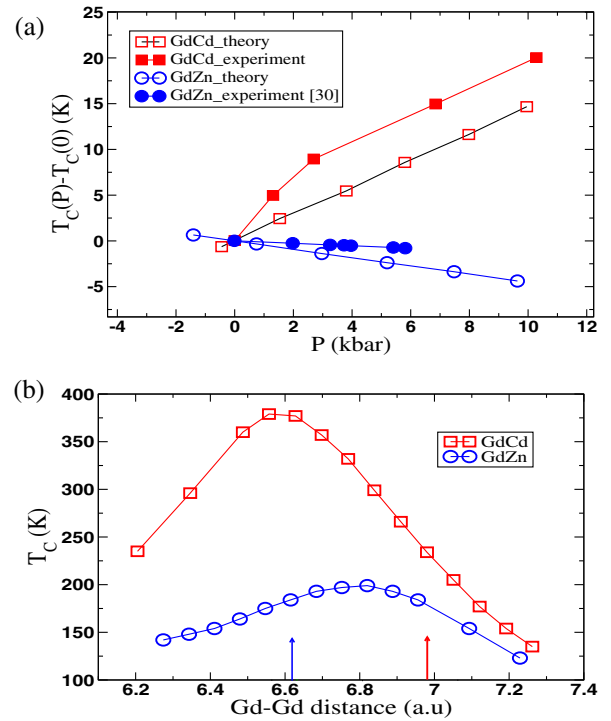


FIG. 1 (color online). (a) Comparison between theory (open symbols) and experimental [19] (filled symbols)  $T_c$  differences  $[T_c(P) - T_c(0)]$ , as a function of pressure  $P$  for GdZn (blue circles) and GdCd (red squares). The experimental data for GdZn are from Ref. [30]. (b)  $T_c$  of GdZn (blue circles) and GdCd (red squares) as a function of lattice parameter  $a$  (atomic units) calculated from the theory. The vertical arrows indicate  $a_{\text{th}}$ , red for GdCd and blue for GdZn.

are simply more extended than the  $3d$ 's of Zn. Our calculations, however, show something rather different. While both theory and experiment find GdCd to be a simple ferromagnet like GdZn, with  $T_c = 234$  K ( $a_{\text{th}} = 6.98$  a.u.) and 265 K [32] ( $a_{\text{exp}} = 7.09$  a.u. [19]), in sharp contrast to its results for GdZn, the theory predicts its  $T_c$  to increase quite dramatically with pressure (Fig. 1), i.e., a positive and rather large  $dT_c/dP$ . Owing to the paucity of reliable published experimental pressure data for GdCd [33], we have carried out measurements [19] to test this specific prediction, and a comparison between the calculated and experimentally observed  $T_c$ 's for GdCd as a function of pressure is shown in Fig. 1(a).

The theory-experiment agreement is excellent:  $dT_c/dP$  from theory is  $+1.5$  and from experiment is  $+1.6$  K kbar $^{-1}$ . While not unusual for first-order magnetostructural transitions (e.g.,  $\approx 1-3$  K kbar $^{-1}$  is observed in  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  alloys [34]), this is a rather high rate for a second-order transition as occurs in GdCd. Reasons for this stark difference between GdZn and GdCd are found from our  $T_c$  calculations as a function of lattice parameter  $a$  [Fig. 1(b)]. Starting from large values,  $T_c$  initially increases with decreasing Gd-Gd distance for both GdZn and GdCd, reaching a maximum whence it starts decreasing with

further reduction of the Gd-Gd distance. The  $dT_c/dP$ 's shown in Fig. 1(a) originate from where the two compounds have their equilibrium lattice spacings  $a_{\text{th}}$ , marked by blue (GdZn) and red (GdCd) arrows in Fig. 1(b) [35].

For materials with the same number of valence electrons per atom, the RKKY account of magnetic interactions would be the same. GdMg is isoelectronic with both GdZn and GdCd but with no filled 3d or 4d band of states. This difference leads to our DLM theory finding GdMg's PM state to be qualitatively different than GdZn's and GdCd's. We find a discordant blend of FM and AF1 dominant magnetic correlations in the PM state—the calculated paramagnetic  $\chi(\mathbf{q})$  has two comparable peaks at wave vectors  $(0,0,0)$  and  $(0,0,\frac{1}{2})$  [19] (in units of  $2\pi/a$ ). Which one is stronger depends on the  $a$  values used. At the theory volume [35] [ $a_{\text{th}} = 7.00$  a.u. (c.f.  $a_{\text{exp}} = 7.20$  a.u. [36])], our calculations predict a FM state below  $T_c = 128$  K. Reducing the Gd-Gd separation weakens the FM aspects, and, for example, a 4% decrease leads to an AF1 state instead, below the Néel temperature  $T_N = 87$  K.

We determine the magnetic order that evolves as  $T$  is lowered through the transition temperature to 0 K as a consequence of these competing FM and AF1 effects by using our DLM theory [19] for the first time to describe a magnetically ordered state with a canted structure and repeating the analysis for a number of  $a$  values. We set the order parameters  $\mathbf{m}_i$ 's for the system at various stages of partial onto complete magnetic order to alternate between  $m_f\hat{z} + m_a\hat{x}$  and  $m_f\hat{z} - m_a\hat{x}$  on consecutive Gd layers along the  $(1,0,0)$  direction giving a canting angle between layers of  $\Theta_c = 2 \arctan(m_a/m_f)$  so that the overall magnetization of a system is local moment size  $\mu$  ( $7.3\mu_B$ ) times  $m_f$ .  $m_f \neq 0$ ,  $m_a = 0$ ,  $\Theta_c = 0$  signifies a FM state, and  $m_a \neq 0$ ,  $m_f = 0$ ,  $\Theta_c = 180^\circ$  an AF1 state.

Figure 2(a) summarizes our results. These are the first *ab initio* calculations to show canted magnetism (CM) in GdMg. The figure shows the emergence of a CM from either a FM ( $\Theta_c = 0$ ) or AF1 state ( $\Theta_c = 180^\circ$ ). For low  $T$ ,  $\Theta_c$  ranges from  $70^\circ$  at the theoretical equilibrium lattice constant (0% reduction) through to  $120^\circ$  (4% reduction) before eventually forming an AF1 magnetic structure (angle  $180^\circ$ ) with further reduction. This agrees very well with experiment [37] which finds that, upon lowering the temperature, GdMg orders into a FM state at  $T_c \approx 110$  K and then undergoes a further second-order transition into a canted magnetic ordered state at  $T_F \approx 85$  K [37,38]. At low  $T$  the magnetization  $\approx 5\mu_B$ , a value we have also confirmed with our own experimental measurements. This is indicative of the FM and AF components  $m_f$  and  $m_a$  being roughly the same size, giving a canting angle between  $7\mu_B$ -sized Gd moments of roughly  $90^\circ$ . This state is robust against applied magnetic fields [38] of up to 150 kOe. The experimental results are matched almost exactly by our calculations shown in Fig. 2(a) for a 2% lattice spacing reduction from  $a_{\text{th}}$ . Liu *et al.* [37] also found that under

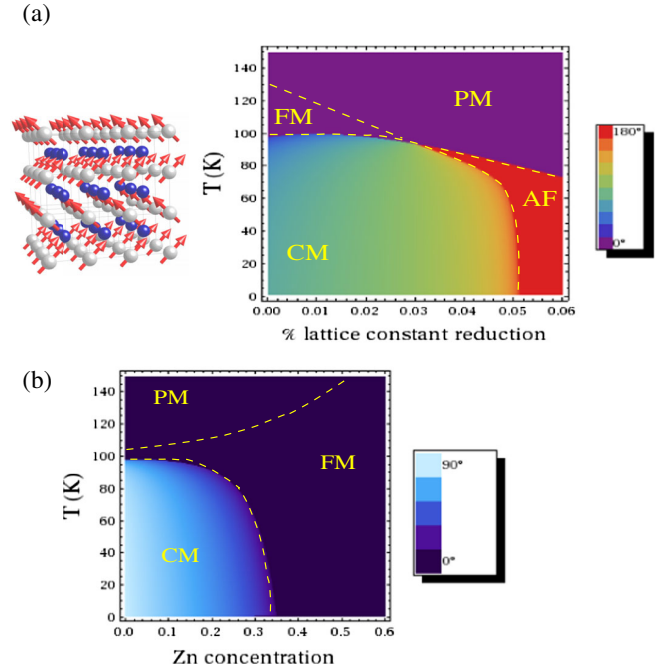


FIG. 2 (color online). (a) The magnetic phase diagram of GdMg, represented by the canting angle  $\Theta_c(T)$  and its dependence on lattice spacing alongside a schematic picture of the CM state. (b) The magnetic phase diagram of  $\text{GdMg}_{(1-x)}\text{Zn}_x$ ,  $\Theta_c(T)$ , and its dependence on  $x$  for a fixed lattice spacing equal to the 2% reduction value in (a), equal to  $a_{\text{th}}$  of  $\text{GdMg}_{0.6}\text{Zn}_{0.4}$ .

pressure GdMg orders into an AF1 from a PM phase at  $\approx 100$  K and at a lower temperature undergoes a further first-order metamagnetic transition into a canted FM phase. The authors estimated the pressure derivative of the magnetization to be  $-0.04\mu_B \text{ kbar}^{-1}$  at 4.2 K, which we have also confirmed experimentally and in fair agreement with our calculated low  $T$  value of  $-0.02\mu_B \text{ kbar}^{-1}$ .

Experimentally, it is known that, when Gd is replaced by Tb in GdMg, there is a 1% lattice contraction [39] and a FM state undergoes a transition into a canted magnetic structure at low  $T$  with  $\Theta_c$  of at least  $90^\circ$ . Replacing Gd with Dy leads to a larger lanthanide contraction, and measurements [40] show that DyMg orders into an AF1 state, developing noncollinear structure with a FM component at low  $T$  and  $\Theta_c$  of about  $110^\circ$ . This correlates with Fig. 2(a) [19] for the smaller lattice spacing regime. The little available data for Ho-Mg [39] also indicate canted AF magnetic structure at low  $T$ . So we infer that the lanthanide contraction [16] in part causes the transition from FM-canted to AF-canted magnetic structures as the heavy lanthanide series is traversed. Our Fig. 2(a) also implies a tricritical point (PM-AF-FM) at some concentration  $y$  in the  $(\text{Tb}_{1-y}\text{Dy}_y) - \text{Mg}$  alloy system with a transition to a canted structure at a marginally lower temperature or possibly a transition into a canted structure directly.

This unusual canted magnetism of GdMg is evidently destroyed by nominally filled, low-lying 3d or 4d bands from the nonlanthanide constituent. Our calculations,

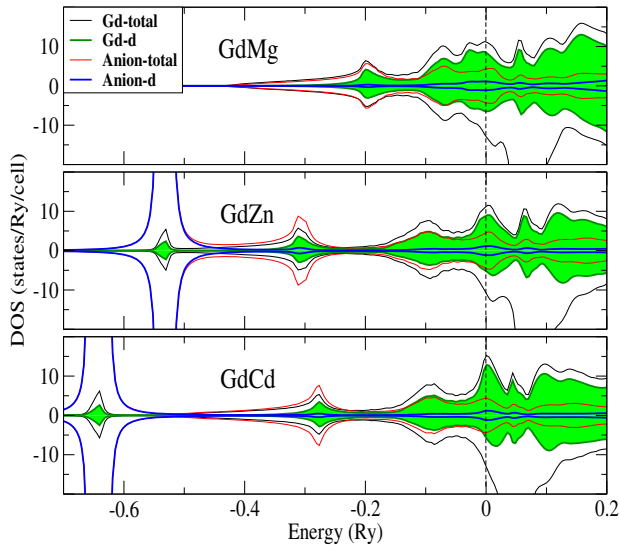


FIG. 3 (color online). The local density of states (DOS) at  $a = a_{\text{th}}$  for the PM states of GdMg, GdZn, and GdCd resolved into Gd (black curve) and Mg,Zn or Cd anion (red) components. The Gd  $d$  component (green curve shaded underneath) and anion  $d$  component (blue curve) are also shown. The upper (lower) panel shows the DOS for an electron spin-polarized parallel (antiparallel) to the local moment on the Gd site. The total DOS, an average over all directions, is unpolarized. The occupied, localized  $4f$  states in each compound are located at  $-1.2$  Ry and are not shown. The narrow structures at  $-0.53$  and  $-0.65$  Ry for GdZn and GdCd, respectively, arise predominantly from the filled Zn/Cd  $d$  states.

Fig. 2(b), show what happens when a fraction  $x$  of the Mg sites in GdMg is replaced by Zn.  $T_c$  increases with  $x$ , and the low-temperature canted structure vanishes altogether for  $x > 0.35$ . This observation is in excellent agreement with the experimental data for GdMg $_{(1-x)}$ Zn $_x$  of Buschow and Oppelt [41], who gave an early report of a serious shortcoming of the RKKY picture.

The successful capturing of these unusual temperature and pressure trends of the Gd intermetallics' magnetism is a consequence of the theory's detailed description of the valence electrons. The theory includes both the response of these electrons to the magnetic ordering of the  $f$ -electron local moments as well as their effect upon it. Figure 3 shows the non-free electron-like PM valence DOS of GdMg, GdZn, and GdCd at  $a_{\text{th}}$  for an electron spin-polarized parallel and antiparallel to the local moment on the Gd site [14]. Averaged over equally weighted moment orientations, the DOS is unpolarized overall. Below  $T_c$ , the electronic structure adjusts and spin-polarizes [19] when magnetic order develops. The Gd  $f$ -moment interactions are properties of the electronic structure around the Fermi energy  $\varepsilon_F$ . The Fermi surface (FS) of PM GdMg (for  $a = 0.96a_{\text{th}}$ ) [Fig. 4(a)] shows a distinctive box structure so that a wave vector,  $(0, 0, \frac{1}{2})$ , connects (nests) [42–44] large portions of parallel FS sheets and drives AF1 magnetic correlations. This topological feature is absent in GdZn's and GdCd's

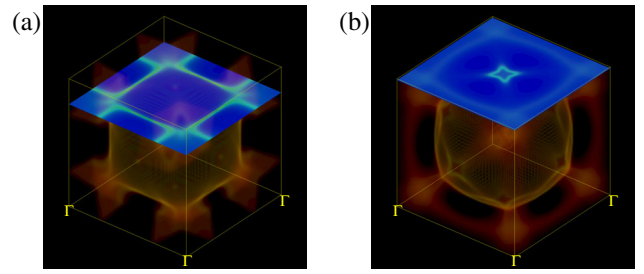


FIG. 4 (color online). The 3D Fermi surface for (a) PM GdMg [ $a = 0.96a_{\text{th}}$ , where Fig. 2(a) shows AF1 order] which shows nesting, and (b) PM GdCd [ $a = 0.94a_{\text{th}}$ , close to Fig. 1(b)'s peak position] showing the “hot spot” at wave vectors  $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ . The finite width of the FS features reflects the local moment disorder. (Constant  $k_z$  slices through the FS are highlighted in blue.)

FSs. Weak hybridization between Gd- $5d$  and lower-lying, nominally filled Zn- $3d$  or Cd- $4d$  states, shown in Fig. 3, causes complex differences between their electronic structures around  $\varepsilon_F$  and GdMg's. In GdZn the Zn  $3d$  bands are narrower than GdCd's  $4d$  ones and lie at slightly higher energies [19]. Moreover, we find that lattice compression increases Gd  $d$ -state occupation relative to  $sp$  ones in these compounds [45,46] which affects FS topology. In particular, as shown in Fig. 4(b) for GdCd, we find that Fig. 1(b)'s peak correlates with a distinct electronic topological transition—a hot spot formed by a hole pocket around  $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ , collapsing as  $a$  is reduced. A similar but much less intense feature is also evident in GdZn's FS.

Atomically localized  $f$  electrons and their intricate physics are inevitably the focus for lanthanide material studies. But the valence electron glue in which the  $f$  moments sit also harbors surprises. Its  $s$ ,  $p$ , and  $d$  electrons can shift it far from a nearly free electron model, as exemplified by the canted magnetism of GdMg and the stark contrast of the magnetism of isoelectronic GdZn and GdCd with their disparate pressure variations. The predictive *ab initio* computational modeling described here has successfully accounted for the subtle aspects of the valence electrons' spin polarizability around  $\varepsilon_F$  and how it is affected by occupation of lower-lying lanthanide-other metal  $d$ -electron bonding states. This implies that further successful quantitative modeling of the rich variety of technologically useful lanthanide-transition metal materials must also treat valence electronic structure accurately and in quantitative detail. We have shown that coordinated *ab initio* theory-experimental studies have the capability of producing new guidelines for understanding the magnetism in lanthanide-transition metal magnets. Factors such as the average number of valence electrons or band filling, separation in energy of the lanthanide  $5d$ , and the other constituents'  $d$  bands and the valence band widths, reminiscent of the modern analogs of the famous Hume-Rothery rules [47] for alloy phase stability, will influence the nature of the valence electron structure around  $\varepsilon_F$  and the magnetism it supports.

We acknowledge the late W. M. Temmerman for valuable and insightful discussions during the early stages of this work. The work was supported by the United Kingdom EPSRC by Grant No. EP/J06750/1 and an EPSRC service level agreement with the Scientific Computing Department of STFC. Work at Ames Laboratory was supported by the Materials Sciences and Engineering Division of the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University.

\*j.b.staunton@warwick.ac.uk

- [1] E. Burzo, *Rep. Prog. Phys.* **61**, 1099 (1998).
- [2] *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner, Jr., L. R. Eyring, J.-C. Bünzli, and V. K. Pecharsky (Elsevier, New York, 1979–2014), Vols. 1–46.
- [3] T. Kasuya, *Prog. Theor. Phys.* **16**, 45 (1956).
- [4] I. A. Campbell, *J. Phys. F* **2**, L47 (1972).
- [5] A. V. Postnikov, V. P. Antropov, and O. Jepsen, *J. Phys. Condens. Matter* **4**, 2475 (1992).
- [6] K. H. J. Buschow, G. E. Grechnev, A. Hjelm, Y. Kasamatsu, A. S. Panfilov, and I. V. Svechkarov, *J. Alloys Compd.* **244**, 113 (1996).
- [7] S. Khmelevskiy, I. Turek, and P. Mohn, *Phys. Rev. B* **70**, 132401 (2004).
- [8] J. Jensen and A. R. Mackintosh, *Rare Earth Magnetism* (Clarendon, Oxford, 1991).
- [9] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [10] M. R. Pederson, R. A. Heaton, and C. C. Lin, *J. Chem. Phys.* **82**, 2688 (1985).
- [11] P. Strange, A. Svane, W. M. Temmerman, Z. Szotek, and H. Winter, *Nature (London)* **399**, 756 (1999).
- [12] L. Petit, R. Tyer, Z. Szotek, W. M. Temmerman, and A. Svane, *New J. Phys.* **12**, 113041 (2010).
- [13] L. Petit, A. Svane, Z. Szotek, P. Strange, H. Winter, and W. M. Temmerman, *J. Phys. Condens. Matter* **13**, 8697 (2001).
- [14] B. L. Gyorffy, A. J. Pindor, J. B. Staunton, G. M. Stocks, and H. Winter, *J. Phys. F* **15**, 1337 (1985).
- [15] M. Lüders, A. Ernst, M. Däne, Z. Szotek, A. Svane, D. Ködderitzsch, W. Hergert, B. L. Györfy, and W. M. Temmerman, *Phys. Rev. B* **71**, 205109 (2005).
- [16] I. D. Hughes, M. Däne, A. Ernst, W. Hergert, M. Lüders, J. Poulter, J. B. Staunton, A. Svane, Z. Szotek, and W. M. Temmerman, *Nature (London)* **446**, 650 (2007).
- [17] J. B. Staunton and B. L. Gyorffy, *Phys. Rev. Lett.* **69**, 371 (1992).
- [18] J. B. Staunton, L. Szunyogh, A. Buruzs, B. L. Gyorffy, S. Ostanin, and L. Udvardi, *Phys. Rev. B* **74**, 144411 (2006).
- [19] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.115.207201> for further information about DLM theory, additional supporting electronic structure calculations and details of the experimental measurements on GdCd, which includes Refs. [20–23].
- [20] H. Ebert, D. Ködderitzsch, and J. Minár, *Rep. Prog. Phys.* **74**, 096501 (2011).
- [21] J. Staunton, B. L. Gyorffy, G. M. Stocks, and J. Wadsworth, *J. Phys. F* **16**, 1761 (1986).
- [22] B. L. Gyorffy and G. M. Stocks, *Phys. Rev. Lett.* **50**, 374 (1983).
- [23] J. S. Faulkner and G. M. Stocks, *Phys. Rev. B* **21**, 3222 (1980).
- [24] J. B. Staunton, A. Marmodoro, and A. Ernst, *J. Phys. Condens. Matter* **26**, 274210 (2014).
- [25] J. B. Staunton, R. Banerjee, M. dos Santos Dias, A. Deak, and L. Szunyogh, *Phys. Rev. B* **89**, 054427 (2014).
- [26] J. B. Staunton, M. dos Santos Dias, J. Peace, Z. Gercsi, and K. G. Sandeman, *Phys. Rev. B* **87**, 060404(R) (2013).
- [27] V. K. Pecharsky and K. A. Gschneidner, Jr., *Cryocoolers* **10**, 629 (1999).
- [28] J. Ruzs, I. Turek, and M. Diviš, *J. Alloys Compd.* **408–412**, 930 (2006).
- [29] B. Sanyal, C. Antoniak, T. Burkert, B. Krumme, A. Warland, F. Stromberg, C. Praetorius, K. Fauth, H. Wende, and O. Eriksson, *Phys. Rev. Lett.* **104**, 156402 (2010).
- [30] T. Hiraoka, *J. Phys. Soc. Jpn.* **37**, 1238 (1974).
- [31] K. Kanematsu, G. T. Alfieri, and E. Banks, *J. Phys. Soc. Jpn.* **26**, 244 (1969).
- [32] G. T. Alfieri, E. Banks, K. Kanematsu, and T. Ohoyama, *J. Phys. Soc. Jpn.* **23**, 507 (1967).
- [33] K. H. J. Buschow, G. E. Grechnev, A. Hjelm, Y. Kasamatsu, A. S. Panfilov, and I. V. Svechkarov, *Physica (Amsterdam)* **237B–238B**, 570 (1997).
- [34] Y. C. Tseng, D. Haskel, J. C. Lang, S. Sinogeikin, Ya. Mudryk, V. K. Pecharsky, and K. A. Gschneidner, *Phys. Rev. B* **76**, 014411 (2007).
- [35] A. Delin, L. Fast, B. Johansson, O. Eriksson, and J. M. Wills, *Phys. Rev. B* **58**, 4345 (1998). We note that this work shows that the generalized gradient approximation gives equilibrium lattice constants in closer agreement with experimental values than the local density approximation.
- [36] P. Manfrinetti and K. A. Gschneidner, Jr., *J. Less-Common Met.* **123**, 267 (1986).
- [37] M. L. Liu, M. Kurisu, H. Kadomatsu, and H. Fujiwara, *J. Phys. Soc. Jpn.* **55**, 33 (1986).
- [38] P. Morin, J. Pierre, D. Schmitt, and D. Givord, *Phys. Lett. A* **65**, 156 (1978).
- [39] R. Aleonard, P. Morin, J. Pierre, and D. Schmitt, *J. Phys. F* **6**, 1361 (1976).
- [40] M. Belakhovsky, J. Chappert, and D. Schmitt, *J. Phys. C* **10**, L493 (1977).
- [41] K. H. J. Buschow and A. Oppelt, *J. Phys. F* **4**, 1246 (1974).
- [42] L. M. Roth, H. J. Zeiger, and T. A. Kaplan, *Phys. Rev.* **149**, 519 (1966).
- [43] S. Dugdale, *Low Temp. Phys.* **40**, 328 (2014).
- [44] K. M. Döbrich, A. Bostwick, J. L. McChesney, K. Rossnagel, E. Rotenberg, and G. Kaindl, *Phys. Rev. Lett.* **104**, 246401 (2010).
- [45] D. G. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford University, New York, 1995).
- [46] G. E. Grechnev, A. S. Panfilov, I. V. Svechkarov, K. H. J. Buschow, and A. Czopnik, *J. Alloys Compd.* **226**, 107 (1995).
- [47] *Alloy Phase Stability*, edited by G. M. Stocks and A. Gonis, NATO ASI Series Vol. 163 (Kluwer Academic Publishers, The Netherlands, 1989).