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Adequacy of the local-spin-density approximation for Gd

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Highly converged local-spin-density-approximation (LSDA) calculations for ferromagnetic hcp Gd have been perfomed using an extended general-potential linearized augmented-plane-wave method. These calculations are used to assess the adequacy of the LSDA for this material. It is found that, while the calculated ground-state properties are in better agreement with experiment than is the case for elements with open $4f$ shells, the LSDA does not provide a fully satisfactory description of this material. On the other hand, an analysis of the electronic structure suggests that a model with localized f electrons is unsuitable for Gd.

I. INTRODUCTION

The utility of the local-spin-density approximation (LSDA) as an accurate and computationally tractable starting point for studies of condensed matter systems is now well established. It is also now established that there are systems for which the LSDA is inadequate. One of the more clear examples of this occurs for the $4f$-band materials. In these materials the LSDA overestimates the extent of the $4f$ itinerancy and as a result the amount of $4f$ bonding. This leads to the LSDA predictions of structural and other ground-state properties in relatively poor agreement with experiment for many, but not all, of these materials.[1-5]

La, Eu, Gd, Yb, and Lu differ from the rest of the lanthanides in that they have closed $4f$ shells. The LSDA predictions of the properties of La,[6] which has no $4f$ electrons, and Lu, which has a full $4f$ shell,[7] are in quite good agreement with experiment. The electronic structures of Eu and Yb are quite different from the other lathanides in that they have approximately one fewer non-f valence electrons per atom. This is a result of the high stability of closed atomic f shells and is reflected in the very soft lattices of these two metals. LSDA calculations using a linearized muffin-tin orbital method reproduce the softness and the closed f shells of these materials. There are, however, possibly important quantitative differences from experiment.[2] In view of the complications which arise from the treatment of the extended $5p$ core states in lathanides and the extreme softness of Eu and Yb, it is unclear to what extent these differences reflect the limitations of the LSDA and to what extent they arise from the necessarily approximate computational approach. It should be noted that, in the case of Eu, calculations were performed for a ferromagnetic bcc structure rather than the actual antiferromagnetic structure.

Gd has an electronic structure more typical of the lanthanides; that is, it has approximately three non-f valence electrons per atom. This leaves seven f electrons. Gd is, in fact, a strong ferromagnet with a magnetization of over $7\mu_B$/atom. Thus, like Lu, Gd has a closed f shell, which, in this case, is fully spin polarized. This may be expected to lead directly to a suppression of f-electron bonding, but not necessarily of f-electron itinerancy. The magnetism leads to a further complication, since there are few tests of the LSDA in the high-density strong spin-polarization regime which occurs in the f shells of Gd. There are, however, indications that the LSDA may be somewhat less reliable in magnetic systems than in nonmagnetic systems. As an example, the LSDA predicts the wrong ground state for iron.[8] Thus, one is led to the question of the accuracy of the LSDA for Gd. This has been the subject of some controversy.

There have been two self-consistent calculations of the structural properties of hcp Gd. Sticht and Kubler,[9] who used an augmented-spherical-wave method, obtained a Wigner-Seitz radius, r_{WS}, 3 or 1.2% smaller than the experimental value depending on whether the total energy or pressure was calculated. More recently, Temmerman and Sterne,[10] using an LSDA-based linearized muffin-tin orbital method, obtained a value of r_{WS} 3.4% smaller than experiment, but also found a very large sensitivity to the treatment of the extended $5p$ core state. By changing the treatment of the $5p$ state, they found that they could change the calculated lattice parameters by over 7%. An error in r_{WS} of 3.4% is outside the expected range for the LSDA errors for systems for which this approximation is accepted as being adequate, and thus the above result would imply that caution is needed in using the LSDA for Gd. The sensitivity to the treatment of the $5p$ state, however, suggests that a calculation with this ambiguity removed is needed to properly assess the adequacy of the LSDA for Gd.

The issue of whether Gd is best described by a model with itinerant f electrons or a model in which the f electrons are localized has been addressed through calculations of magnetic and electronic properties. Sticht and Kubler argued that an itinerant model is appropriate for Gd. This was based on the reasonable agreement of the magnetization calculated within the LSDA with the experimental value and the surprisingly large polarization of the valence s-d electrons and consequent disagreement with experiment in a localized f-electron model.[9] Subsequently, Richter and Eschrig[11] repeated these calculations using a different technique and found that the large

polarization of the valence electrons in the localized model of Sticht and Kubler was probably an artifact. They argued that a localized model of the Gd f electrons was preferable. This conclusion was based on their finding of a lower gyromagnetic ratio, g, with localized f electrons, seemingly in better agreement with experiment than the higher LSDA value. Krutzen and Springelkamp,[12] however, found that relativistic effects reduce g in an itinerant model to a value near that for a localized model and that, given the accuracy of the experimental data, the two pictures cannot be distinguished on this basis.[12–14]

Since the pioneering work of Dimmock and Freeman,[15] there have been a number of band-structure calculations for Gd. Self-consistent calculations for the hcp crystal structure yield electronic densities of states (DOS) at the Fermi level, $N(E_F)$, spanning a wide range (25–47 states/Ry),[9,10,12,16] with all calculations yielding values larger than the experimental value of 21 states/Ry.[17] This is unusual since, normally, the electron-phonon coupling and electronic correlations both lead to enhancements of $N(E_F)$ above the bare LSDA value. Temmerman and Sterne[10] have compared calculated Fermi surfaces with de Haas–van Alphen (dHvA) measurements[18] obtaining qualitative agreement for the s-d transition-metal-like sheets. However, they did not find several small area sections which were observed experimentally. Further, just as for the ground-state properties, they found that the calculated band structures near the Fermi energy was quite sensitive to the treatment of the 5p core state.

Clearly, additional calculations are required to resolve, first of all, whether a localized or itinerant model of the f electrons is appropriate, and secondly whether or not the LSDA provides an adequate description of this material. Here highly converged LSDA-based calculations for Gd are presented. To our knowledge these are the first self-consistent full-potential calculations for Gd. The issue of localization versus itinerancy of the f electrons is discussed in terms of the calculated electronic structure and that of the adequacy of the LSDA in terms of the calculated ground-state properties.

II. METHOD

As mentioned, the treatment of the 5p core states can significantly affect the results of calculations for Gd. La is a useful reference system for the 4f-band metals since it has an identical electronic structure with the exception that it has no f electrons. Calculations for La have shown that, as in the case of Gd, there are significant residual errors due to the treatment of the 5p state even in highly converged two-window general-potential linearized augmented-plane-wave (LAPW) calculations.[6] In the present study, a local orbital extension[6] of the LAPW method[19] is used to treat the Gd 5s and 5p core states accurately. This extension removes the ambiguities associated with these extended core states and yields results in very good agreement with experiment for La. In the present calculation, additional local orbitals were added to the LAPW basis to reduce errors due to the linearization of the narrow f bands in Gd.

The calculations were performed using a Gd sphere radius, $R_{MT}=3.1$ a.u. and a basis set determined by a maximum plane-wave vector, $K_{max}=10.5/R_{MT}$. The Brillouin zone was sampled using 90 special **k** points in the irreducible wedge of the hcp zone.[20] Convergence tests were performed using up to 352 special **k** points. Calculations for the fcc structure were performed using a set of 60 special **k** points. Tests indicate that the hcp-fcc energy difference is converged to better than 0.3 mRy per atom with these samplings. The total energy calculations were performed fully self-consistently with the core states being treated (note that the 5s and 5p states are considered valence states for this purpose) fully relativistically in a spherical approximation. The electronic-structure calculation for the experimental lattice parameters was performed self-consistently, including spin orbit in a second variational step, as were a series of total-energy calculations at a fixed c/a ratio. These total-energy calculations showed that the effect of spin orbit on the static structural properties is small, and accordingly a scalar relativistic approximation was used for the valence states in the remainder of the total-energy calculations. The von Barth–Hedin form of the exchange-correlation function was used.[21] The static properties for the fcc structure were obtained by fitting calculated total energies to the Murnaghan equation of state.[22] For the hcp structure, the situation is somewhat more complicated since there are two structural parameters. In order to determine the static properties for this structure, total-energy calculations were performed for 25 sets of c and a lattice parameters. These were fit to a polynomial form including all terms up to third order in the cell volume and c/a ratio plus a fourth-order term consisting of the square of the product of c/a ratio and cell volume. The static properties were extracted from the polynomial coefficients.

III. RESULTS AND DISCUSSION

The principal results of the present calculation are the ground-state properties and electronic structure. These are summarized in Table I, where calculated properties of Gd are compared with experiment and Fig. 1 which is the calculated band structure with the experimental lattice parameters.

A. Band structure: Localization versus itinerancy

As expected,[15] the band structure can be qualitatively described as that of a three-electron per atom transition metal with f bands superimposed. The f bands are separated into two manifolds by an exchange splitting of 5.0 eV. The lower manifold is centered 4.5 eV below E_F and the upper manifold 0.5 eV above E_F, with the result that the upper manifold is unoccupied. The other bands have much smaller exchange splittings. The exchange splittings of the occupied s-d valence bands at Γ are 0.90 and 0.97 eV. Both the occupied and unoccupied f manifolds have a width of 0.7 eV. Much of this width is due to the spin-orbit interaction; scalar relativistic calculations yield widths of 0.2 and 0.4 eV for the occupied and

TABLE I. Calculated properties of Gd. The spin-orbit interaction is included for the electronic properties [M and $N(E_F)$], but not for the structural properties (see text). The calculated value of M is the spin magnetization. The experimental value is the total magnetization (including the orbital component). E (fcc-hcp) is the fcc-hcp structural energy difference.

	This study	Experiment
r_{WS} (a.u.)	3.633	3.762[a]
c/a	1.601	1.597[a]
B (GPa)	38.8	41.3[b]
M	7.57	7.63[c]
$N(E_F)$ (Ry atom)$^{-1}$	27.1	21.35[d]
E (fcc-hcp) (mRy/atom)	0.9	>0[e]

[a]Reference 23 (106 K).
[b]Reference 24.
[c]Reference 14.
[d]Reference 17.
[e]Reference 25.

unoccupied manifolds, respectively. The DOS is similar to that obtained in previous calculations[9,10] and is not shown here. The calculated value of $N(E_F)$ is 27.1 states/Ry, which is significantly larger than the experimental value of 21.35. The f component of $N(E_F)$ is 5 states/Ry and is almost entirely minority spin in character. This is evidence that, at least in the LSDA, there is significant hybridization of the upper f manifold with the transition-metal bands which disperse through it. Further evidence of this is apparent in dispersions of the bands at and above E_F. This is in accord with the results of earlier relativistic calculations.[9,10] There are, however, differences near the Fermi energy, and these are important. In particular, the position of the structure in the bands with respect to E_F differs, with the result that there are additional bands crossing E_F in the present calculation. This leads to additional small Fermi surfaces around M and K. This is important in view of the small Fermi surfaces observed experimentally,[18] but not found in previous calculations. It should be noted that the areas of the small Fermi surfaces found in the present calculation depend strongly on the position of the Fermi energy. (A 40-meV shift in either direction will change the topology.) While the present calculation is sufficiently well converged to establish the existence of these Fermi surfaces, it is premature to attempt a detailed comparison with dHvA frequencies. The complex structure of the bands near E_F reflects the hybridization of the valence bands with the upper f manifold. This is to be expected from the relatively large f component of the DOS at E_F and the sensitivity of the Fermi surface topology to the placement of E_F. An examination of the characters of the bands crossing E_F along $\Gamma-M$ and near K supports this. These bands have differing orbital characters and differing amounts of f character. The flat band, which has two Fermi-surface crossings along $\Gamma-M$, is predominantly majority spin in character and has only a small f component. On the other hand, the band crossing E_F near K is predominantly minority spin in character and has a significant f component. At K, over 16% of the weight of this band is minority spin f-like. Hybridization with the f electrons and the resulting complexity of the Fermi surfaces would not be present in a model with localized f electrons. Thus, the presence of small-area Fermi surfaces in both experiment and the present calculation indicates that a model with f-electron itinerancy is needed to describe the electronic structure of Gd.

B. Ground state: Adequacy of the LSDA

LSDA band structures are often in reasonable accord with experiment and LSDA Fermi surfaces often agree very well with dHvA measurements, even for some quite strongly correlated materials. It should be noted, however, that the LSDA is a ground-state theory, and accordingly, in order to test the applicability of the LSDA to a given material it is necessary to examine ground-state properties. The ground-state properties calculated in the present study are the structure (r_{WS} and c/a), the bulk modulus B, and the magnetization M. As may be noted from Table I, the overall agreement of these quantities

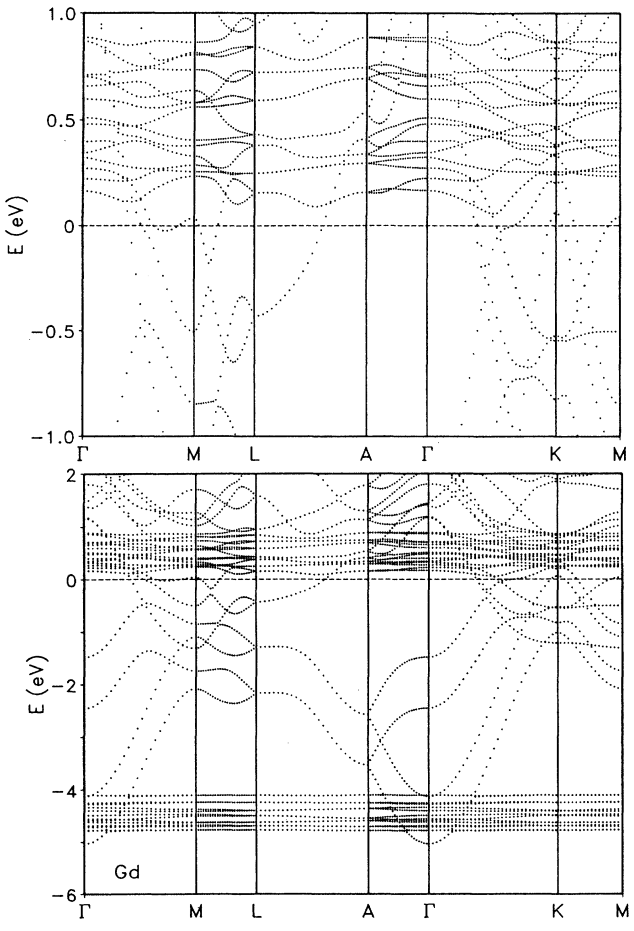

FIG. 1. LSDA band structure of Gd at the experimental structure. The upper panel is a blowup of the band structure near the Fermi energy.

with experiment is fair at best. The magnetization is similar to that obtained in previous studies and quite close to the experimental value. Adding an orbital component to the calculated magnetization is expected to increase it by between $0.04\mu_B$/atom and $0.05\mu_B$/atom (Ref. 12) yielding nearly perfect agreement with experiment. However, because of the nearly complete polarization of the f shell, the magnetization is not as sensitive a test of the LSDA as are the other ground-state properties. When calculated in a scalar relativistic approximation, r_{WS} is 3.4% smaller than the experimental value and the bulk modulus is 6% smaller than experiment. The calculated fcc-hcp structural energy difference is 0.9 mRy/atom, in agreement with the observed hcp structure. As mentioned, in order to determine the effect of the scalar relativistic approximation, a series of total-energy calculations including spin orbit were performed at a fixed c/a ratio. These calculations were performed at $c/a = 1.591$, which is close to the experimental value. The result of this test is that the effect of the spin orbit is small and in the *wrong* direction to improve agreement with experiment. With spin-orbit interactions included, r_{WS} was found to be 0.4% smaller than in a scalar relativistic approximation. This contraction of the lattice can be understood in terms of the band structure. The dominant effect of spin orbit is to broaden the f bands. Broadening the minority-spin f manifold brings the f bands closer to E_F and consequently increases the amount of f hybridization in the bands at E_F. This leads to an increase in the participation of the f electrons in the bonding and a contraction of the lattice.

IV. CONCLUSIONS

Well-converged calculations of the electronic structure and ground-state properties of Gd have been performed within the LSDA. Several small Fermi-surface sections are found in the present calculation which were not present in earlier calculations. Since small-area Fermi-surface sections are observed experimentally, and in the calculation these depend on the hybridization of the minority spin f electrons and the transition-metal-like bands, it is argued that the f electrons have itinerant character in Gd. On the other hand, the agreement of the LSDA ground-state properties with experiment is marginal. In particular, the error in the lattice parameters, while not as large as found in calculations for other lanthanides,[1-5] is large enough to lead to the conclusion that the LSDA does not provide a fully satisfactory description of Gd.

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