Stability of the Gd magnetic moment to the 500 GPa regime: An LDA+U correlated band method study

Z. P. Yin and W. E. Pickett
Department of Physics, University of California, Davis, California 95616, USA
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The evolution of the magnetic moment and various features of the electronic structure of fcc Gd are followed to reduced volume $V/V_o=0.125$ using the LDA+U correlated band method. The stability of the moment is substantial; crude estimates of this signature of a possible "Mott transition" in the $4f$ system suggest a critical pressure $P_c \sim 500$ GPa. The $4f$ occupation is found to *increase* under pressure due to broadening and lowering of the minority states. This trend is consistent with the interpretation of x-ray spectra of Maddox *et al.* across the volume collapse transition at 59 GPa, and tends to support their suggestion that the delocalization of the $4f$ states in Gd differs from the original abrupt picture, being instead a process that occurs over an extended range of pressure.

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I. INTRODUCTION

The behavior of the $4f$ rare-earth metals and their compounds under pressure has been discussed for decades, with the volume collapse transition under pressure attracting a great deal of attention. It has been known for some time that there are volume collapse transitions in Ce (15% at 0.7 GPa), Pr (10% at 20 GPa), Gd (5% at 59 GPa), and Dy (6% at 73 GPa), while no significant volume collapses have been detected in Nd, Pm, and Sm. The equation of state of these metals, and references to the original work, has been collected by McMahan *et al.*[1] High-temperature experiments[2] have seen signatures that are likely related to the localized $\rightarrow$itinerant transition, at 50 GPa in Nd and 70 GPa in Sm.

The question can be stated more generally as: what form does the localized$\rightarrow$itinerant transition of the $4f$ states take, and what is the correct description? This transition is intimately related to the question of behavior of magnetic moments,[1] although the questions are not the same. There have been two main viewpoints on the volume collapse transition. One is the "Mott transition of the $4f$ system" elaborated by Johansson,[3] in which the crucial ingredient is the change from localized (nonbonding) to more extended states (participating in bonding), with an accompanying drop in magnetic tendency. The other is the "Kondo volume collapse" view introduced by Allen and Martin[4] and Lavagna *et al.*,[5] in which the main feature is the loss of Kondo screening of the local moment, with a decrease in localization of the $4f$ state not being an essential feature.

At ambient conditions the $4f$ electrons form a strongly localized f^n configuration that is well characterized by Hund's rules. Under reduction of volume, several things might be anticipated to happen. At some point the $4f$ system begins to respond to the nonspherical environment. Initially, perhaps, it is just a matter of crystal-field splitting becoming larger. Then the $4f$ orbitals actually begin to become involved in the electronic structure, by overlapping orbitals of neighboring atoms. The consequences of this are possible participation in bonding, and that the orbital moment becomes less well defined (the beginning of quenching, i.e., the loss of Hund's second rule, which has already occurred in magnetic $3d$ systems). Additionally, the $4f$ levels can shift and increase their interaction with the itinerant conduction (c) bands (Kondo-like coupling), which can change the many-body behavior of the coupled $4f$-c system. At some point the kinetic energy increase, characterized by the $4f$ bandwidth W_f, compared to the on-site interaction energy U_f reaches a point where the spin moment begins to decrease. Finally, at small enough volume (large enough W_f) the $4f$ states simply form nonmagnetic conduction bands.

Just how these various changes occur, and in what order and at what volume reduction, is being addressed in more detail by recent high-pressure experiments. Here we revisit the case of Gd, whose volume collapse was reported by Hua *et al.*[6] and equation of state by Akella *et al.*[7] The deviation from the series of close-packed structures below $P_c=59$ GPa and the lower symmetry bcm (body-centered monoclinic) high-pressure structure signaled the expected onset of f-electron participation in the bonding, and Hua *et al.* seemed to expect that the moment reduction and delocalization of the $4f$ states would accompany this collapse.

New information has been reported by Maddox *et al.*,[8] who have monitored the resonant inelastic x-ray scattering and x-ray emission spectra of Gd through P_c and up to 113 GPa. They find that there is no detectable reduction in the magnetic moment at the volume collapse transition, so the volume collapse is only a part of a more complex and more extended delocalization process of the $4f$ states. Maddox *et al.* emphasize the Kondo-volume-collapse[9,10] aspects of the transition at P_c.

The treatment of the $4f$ shell, and particularly the volume collapse and other phenomena that may arise (see above), comprises a correlated-electron problem for theorists. Indeed there has been progress in treating this volume-collapse, moment-reduction problem in the past few years. The issue of the (in)stability of the local moment seems to involve primarily the local physics, involving the treatment of the hybridization with the conduction bands and interatomic f-f interaction, with Kondo screening of the moment being the subsequent step. Dynamical mean-field studies of the full multiband system have been carried out for Ce,[1,11,12] and for Pr and Nd.[12] These calculations were based on a well-defined

free-energy functional and included the conduction bands as well as the correlated $4f$ bands. One simplification was that only an orbital-independent Coulomb interaction U was treated, leaving the full orbital-dependent interaction (fully anisotropic Hund's rules) for the future. Density-functional based correlated band theories have also been applied (at zero temperature). Self-interaction corrected local-density approximation (LDA) was applied to Ce, obtaining a volume collapse comparable to the observed one.[13] Four correlated band theories have been applied[14] to the antiferromagnetic insulator MnO. Although their predictions for critical pressures and amount of volume collapse differed, all obtained a $S=5/2$ to $S=1/2$ moment collapse rather than a collapse to a nonmagnetic phase.

Clearly there remain fundamental questions about how the magnetic moment in a multielectron atom disintegrates as the volume is reduced: catastrophically, to an unpolarized state, or sequentially, through individual spin flips or orbital-selective delocalization. If the latter, the total (spin+orbital) moment could actually *increase* initially in Gd. If the occupation change is toward f^8, the decrease in spin moment (from $S=7/2$ to $S=3$) could be more than compensated by an orbital moment ($L=3$). If the change is toward f^6, the onset of an $L=3$ orbital configuration could oppose the $S=3$ spin (Hund's third rule), leaving a nonmagnetic $J=0$ ion (as in Eu^{3+}) even though the $4f$ orbitals are still localized. Still another scenario would be for the increasing crystal field to quench the orbital moment (as in transition metals) and the remaining problem involves only the spins.

Our objective here is to look more closely at the stability of the Gd atomic moment, in the general context of the localized→itinerant transition of the $4f$ system under pressure. We apply the LDA+U (local-density approximation plus Hubbard U) method to study the evolution of the electronic structure and magnetism as the volume is reduced. Although this correlated band method neglects fluctuations and the dynamical interaction with the conduction electrons, it does treat the full multiorbital system in the midst of itinerant conduction bands. The resulting moment vs volume surely provides only an upper limit to the pressure where the moment decreases rapidly. However, we can invoke studies of the insulator-to-metal transition in multiband Hubbard models to provide a more realistic guideline on when the localized→itinerant (or at least the reduction in moment transition within the $4f$ system may be expected to occur). The results suggest stability of the moment to roughly the 500 GPa region.

II. ELECTRONIC STRUCTURE METHODS

In the paper we apply the full potential local orbital code[15] (FPLO5.00-18) to Gd from ambient pressure to very high pressure (a few TPa). We use the fcc structure with space group $Fm3m$ (225) and ambient pressure (corresponding to the fcc lattice constant $a_0=5.097$ Å). The basis set is (core)::$(4d4f5s5p)/6s6p5d+$. We use 48^3 k-point mesh and Perdew and Wang's W92 functional[16] for exchange and correlation. We have tried both 5.0 and 6.0 for the confining potential exponent, with very similar results, so only the results using exponent=5 will be presented here. We perform both LDA and LDA+U calculations (see below). Due to the extreme reduction in volume that we explore, any band-structure method might encounter difficulties. For this reason we have compared the FPLO results on many occasions with parallel calculations with the full-potential linearized augmented plane-wave method WIEN2K.[17] The results compared very well down to $V/V_o=0.5$, beyond which the WIEN2K code became more difficult to apply. We use the notation $v \equiv V/V_o$ for the specific volume throughout the paper.

A. LDA+U method

For the strength of the $4f$ interaction we have used the volume dependent $U(V)$ calculated by McMahan *et al.*,[1] which is shown below. Due to the localized $4f$ orbital and the large atomic moment, we use the "fully localized limit" version of LDA+U as implemented in the linearized augmented plane-wave method,[18] and as usual the ratio of Slater integrals is fixed at $F_4/F_2=0.688$, $F_6/F_2=0.495$. Since we are particularly interested in the stability of the atomic moment, the exchange integral J that enters the LDA+U method deserves attention. In atomic physics, and in the LDA+U method, the exchange integral plays two roles. It describes the spin dependence of the Coulomb interaction, that is, the usual Hund's rule coupling. In addition, it carries the orbital off-diagonality; with $J=0$ all $4f$ orbitals repel equally by U, whereas in general the anisotropy of the orbitals leads to a variation[19] that is described by J.

For a half filled shell for which the orbital occupations $n_{m\uparrow}=1$ and $n_{m\downarrow}=0$ for all suborbitals m, the exchange effect primarily counteracts the effect of U, since the anisotropy of the repulsion averages out. As a result, using $U_{eff} \equiv U-J$ with $J_{eff}=0$ is almost equivalent, for a perfectly half-filled shell, to using U and J separately as normally is done. This result is readily seen from the following form of the additional energy in the LDA+U functional (exact when the occupation matrix n is diagonal):

$$E_U = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} [U_{mm'} - \delta_{\sigma,\sigma'} J_{mm'}](n_{m\sigma} - \bar{n}_s)(n_{m'\sigma'} - \bar{n}_{s'}). \tag{1}$$

Here $\bar{n}_\sigma$ is the mean occupation of spin σ. For Gd (at least until very high pressure) $n_{m\sigma} \approx \bar{n}_\sigma$ (all majorities are fully occupied, all minorities are nearly empty) so the change in energy will be small for Gd. Below we indicate the extremely small differences as U and J are changed.

Since it could be argued that Hund's first rule is treated adequately by the LDA exchange-correlation functional, for our calculations we have set $J=0$. This becomes approximate for the off-diagonality effects when the minority $4f$ states begin to become occupied at high pressure. However, we have checked the effect at $a/a_o=0.8$ ($v=0.5$, $P=60$ GPa). Using $J=0$ vs 1 eV with $U=5.9$ eV leaves the energy unchanged (at the mRy level), while the spin moment is $0.03\mu_B$ larger for $J=0$. Using $U=6.9$ eV, $J=1$ eV gives the same energy and moment as $U=5.9$ eV, $J=0$. At much smaller volumes, where the minority bands overlap the Fermi level,

the changes become noticeable and would affect the EOS somewhat. In addition, note that our neglect of J tends to *underestimate* the stability of the magnetic moment, which we show below already to be extremely stable.

B. Structure

The observed structures of Gd follow the sequence hcp→Sm-type→dhcp→dfcc→bcm (dfcc≡distorted fcc, which is trigonal; bcm≡body-centered monoclinic). All except the bcm phase are close-packed arrangements, differing only in the stacking of hexagonal layers. The bcm phase is a lower symmetry phase that suggests f-electron bonding has begun to contribute.

For our purpose of studying trends relating only to the atomic volume, it is best to stay within a single-crystal structure. We expect the results to reflect mostly local physics, depending strongly on the volume but only weakly on the long-range periodicity. Therefore we have kept the simple fcc structure for the results we present.

III. LDA+U RESULTS

The overall result of our study is that evolution of the volume and the Gd moment are predicted by LDA+U to be continuous under reduction of volume, with no evidence of a volume-collapse transition (or any other electronic phase change) in the region where one is observed (59 GPa), or even to much higher pressure. This result provides some support for the suggestion that the volume collapse is Kondo-driven, or involves in an essential way fluctuations, neither of which are accounted for in our approach.

While we will usually quote volumes or the relative volume v, it is useful to be able to convert this at least roughly to pressure. We provide in Fig. 1 the calculated equation of state, plotted as log P vs V/V_o. It can be seen that the pressure is very roughly exponential in $-V/V_o$ from $v=0.8$ down to $v=0.15$ (2 GPa–4 TPa). The change in slope around $v=0.4$ (in the vicinity of 100–200 GPa) is discussed below.

A. Magnetic moment vs volume

The behavior of the total spin moment ($4f$ plus conduction) in LDA+U is compared in Fig. 2 with that of LDA. The general trend is similar, but the decrease in moment is extended to smaller volume by the correlations in LDA+U. Specifically, the moment is reduced not by a decrease of majority spin population (which would be $f^7 \rightarrow f^6$) but rather by an increase in the minority spin population ($f^7 \rightarrow f^8$; see discussion below). Thus LDA+U enhances the stability of the moment by raising the unoccupied minority $4f$ states in energy, thus reducing and delaying compensation of the filled majority states. It has been noted elsewhere[21] that raising the minority states is the main beneficial effect of the LDA+U method for Gd at ambient pressure.

The decrease in moment is minor down to $v=0.45$ (~90–100 GPa) beyond which the decrease from $7\mu_B$ to $6\mu_B$ occurs by $v=0.2$ ($P\sim 1$ TGa). Only beyond this incredibly high pressure does the moment decrease more rapidly, as the $4f$ states become bandlike. Even in LDA this collapse

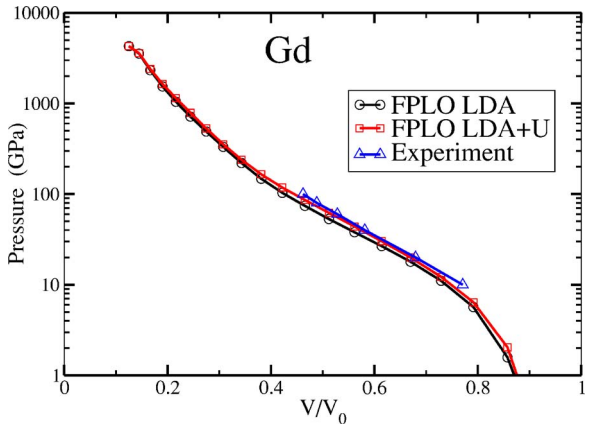

FIG. 1. (Color online) Log plot of the calculated pressure vs volume. The relatively small difference between the LDA+U and LDA results is evident. The relation is roughly exponential below $V/V_o<0.8$. Experimental data from 10 to 100 GPa from Ref. 7 is shown for comparison. Current static diamond-anvil cells will only take Gd to the $V/V_o\sim 0.35$ region. Note: the equation of state over such an extended volume range cannot be fit to standard forms (Birch, Murnaghan, etc.) which provide an expansion around equilibrium. Our curve was obtained from the nonlinear fit provided by the widely used *Grace* (also known as *xmgrace*) graphics package.[20]

does not occur until below $v=0.3$ ($P\sim 300$–400 GPa). With the neglect of fluctuations, the simplistic interpretation of the LDA+U results is that the Gd "bare" spin moment is relatively stable to ~1 TPa.

It might be thought that, for the region of spin moment of $6\mu_B$ and below, where the minority occupation is 1 or more, there might be an orbital moment of the minority system. However, at these volumes (see below) the minority $4f$ bandwidth is 5 eV or more, which we think makes an orbital moment unlikely. Therefore we have not pursued this possibility.

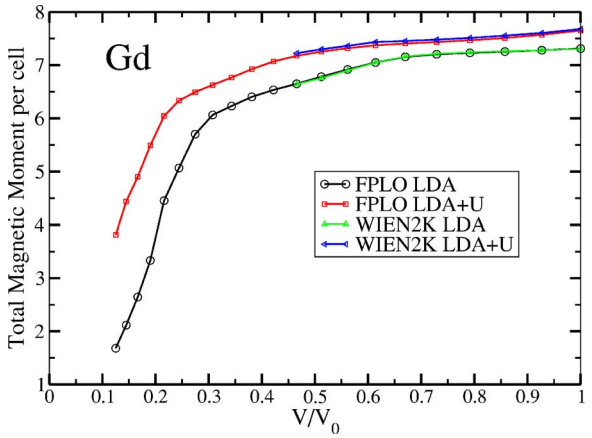

FIG. 2. (Color online) Behavior of the calculated moment per cell ($4f$ spin moment plus conduction electron polarization) of Gd vs reduction in volume, from both LDA and LDA+U methods. For the more realistic LDA+U method, there is very little decrease in moment down to $V/V_o=0.45$ (~110 GPa), with a rapid decline beginning only around $V/V_o\approx 0.2$ (1.5 TPa).

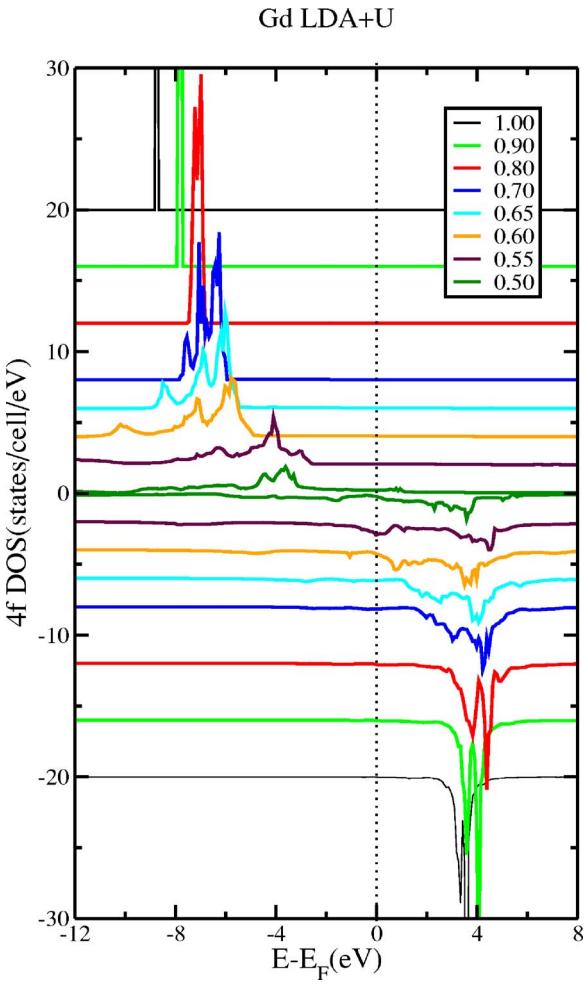

FIG. 3. (Color online) View of the $4f$ projected density of states under compression, with majority spin plotted upward and minority plotted downward. The curves are displaced for clarity, by an amount proportional to the reduction in lattice constant. The legend provides the ratio a/a_o, which is decreasing from above, and from below, toward the middle of the figure.

B. 4*f* bandwidth

The behavior of the $4f$ states, which become bands, is better illustrated in Fig. 3, where the evolution of the $4f$ "bands" [the $4f$ projected density of states (PDOS)] is provided graphically. At $a/a_o=0.80$ ($v=0.51$, $P\approx 60$ GPa, where the volume collapse is observed) the majority PDOS is somewhat less than 2 eV wide and still atomiclike, since it does not quite overlap the bottom of the conduction band. Above this pressure range the $4f$ states begin to overlap the conduction bands, primarily due to the broadening of the conduction bandwidth. By $a/a_o=0.70$ ($v=0.34$, $P\approx 200$ GPa) the width is at least 3 eV and the shape shows the effect of hybridization and formation of bands. For yet smaller volumes the bandwidth becomes less well defined as the bands mix more strongly with the conduction states and broaden. The minority PDOS lies in the midst of Gd $5d$ bands and is considerably broader down to $a/a_o=0.70$, beyond which the difference becomes less noticeable.

The position of the $4f$ states relative to the semicore $5p$, and conduction $5d$ states, and their evolution with volume, are pictured in Fig. 4. The semicore $5p$ bands broaden to $\sim$10 eV by 200 GPa, but it requires supra-TPa pressures to broaden them into the range of the majority $4f$ states. The upturn in the log P vs V curve in Fig. 1 in the vicinity of 100–200 GPa is probably due to $5p$ semicore overlap on neighboring atoms (repulsion of closed shells as they come into contact). The $5d$ bands broaden in the standard way under pressure, and begin to rise noticeably with respect to the $4f$ states beyond 60 GPa.

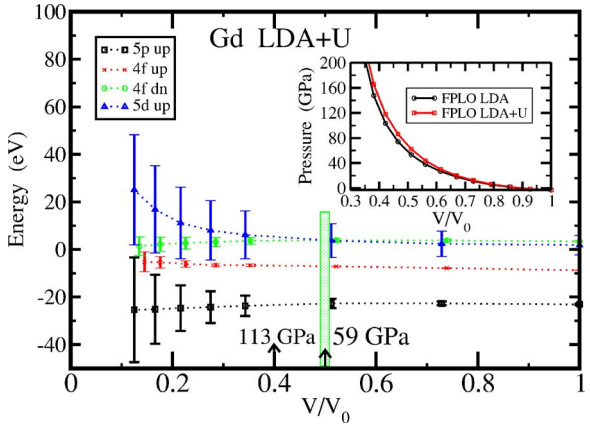

FIG. 4. (Color online) Plot of band positions (lines) and widths (bars) of the majority and minority $4f$ states, the semicore $5p$ bands, and the valence $5d$ bands, for ferromagnetic Gd. The bar at $V/V_o=0.5$ ($\sim$59 GPa) marks the observed volume collapse transition, while the arrow at 113 GPa denotes the highest pressure achieved so far in experiment. These results were obtained from LDA+U method, with U varying with volume as given by McMahan *et al.* (Ref. 1).

The minority $4f$ bands fall somewhat with respect to E_F as they broaden, both effects contributing to an increase in the minority $4f$ occupation at the expense of $5d$ and $6s6p$ character. Since the majority $4f$ states remain full, the effect is that the total f count increases and the spin moment decreases (as discussed above).

The volume dependence of the $4f$ bandwidth in nonmagnetic Gd has been looked at previously by McMahan *et al.*[1] They identified the intrinsic width W_{ff} from the bonding and antibonding values of the $4f$ logarithmic derivative; W_{ff} lies midway (roughly halfway) between our majority and minority bandwidths, see Fig. 4. McMahan *et al.* also obtained a hybridization contribution to the $4f$ width; both of these would be included in our identified widths. Our widths, obtained for ferromagnetically ordered Gd, are difficult to compare quantitatively with those of McMahan *et al.*, because the positions of our minority and majority states differ by 12 eV at $P=0$, decreasing under pressure. Note that our minority and majority widths, obtained visually from Fig. 3 differ by a factor of $\sim$6 at $v=1.0$, still by a factor of 2.5 at $v=0.3$, and only become equal in the $v<0.2$ range.

C. Comments on Mott transition

In the simplest picture (single-band Hubbard model) the Mott transition is controlled by the competition of kinetic (W) and potential (U) energies, with the transition occurring

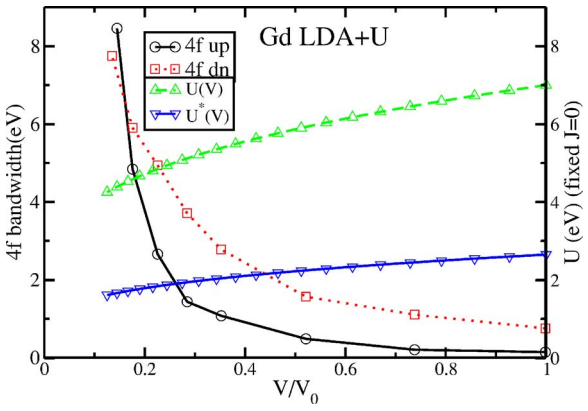

FIG. 5. (Color online) Plot of the $4f$ bandwidths (both majority and minority), together with the volume-dependent Coulomb repulsion U from McMahan (Ref. 1). The simple crossover criterion $W_f \approx U$ occurs around $V/V_o = 0.20-0.25$, corresponding roughly to a pressure of 700–1000 GPa. Also pictured is $U^* \equiv U/\sqrt{7}$, see text for discussion.

around $W \approx U$. This transition is normally pictured as a simultaneous insulator-to-metal, moment collapse, and presumably also volume collapse transition. In Gd, however, no change in moment is observed[8] across the volume collapse transition at 59 GPa.

In Fig. 5 the $4f$ bandwidths (majority and minority bands), and the Coulomb U of McMahan *et al.*[1] are plotted vs volume. The region $W \approx U$ occurs around $v \sim 0.20-0.25$. This volume corresponds to a calculated pressure in the general neighborhood of 1 TPa, indicative of an extremely stable moment well beyond present capabilities of static pressure cells. This criterion, however, presumes a simple single band system, which Gd is not.

Gunnarsson, Koch, and Martin have considered the Mott transition in the multiband Hubbard model,[22–24] and found that the additional channels for hopping favored kinetic processes that reduced the effect of the Coulomb repulsion. They argued that the criterion involved the inverse square root of the degeneracy, which can be characterized by an effective repulsion $U^* = U/\sqrt{7}$ (for f states the degeneracy is $2\ell+1=7$). The Mott transition could then be anticipated in the range $W \approx U^*$, for which $U^*(V)$ has also been included in Fig. 5. Taking W as the average of the majority and minority widths gives the crossover around $v_c \sim 0.35$ ($P_c \sim 200$ GPa); taking W more realistically as the majority bandwidth gives $v_c \sim 0.25$ ($P_c \sim 750$ GPa).

Another viewpoint on the "Mott transition" in the $4f$ system is that it can be identified with the "metallization" of the $4f$ bands, which might be expected to be where the occupied and unoccupied bands overlap. These are, respectively, the majority and minority bands. Significant overlap occurs only above 2 TPa ($v < 0.20$) in Fig. 5. The fact is that metallization (however, defined for a $4f$ system in the midst of uncorrelated itinerant conduction bands) and moment collapse need not coincide, and the concept of Mott transition may need to be generalized.

IV. SUMMARY

In this paper we have applied the correlated band theory LDA+U method to probe the electronic and magnetic character of elemental Gd under pressure. The calculated moment decreases slowly down to $V/V_o = 0.20$ ($P > 1$ TPa), and only at smaller volumes does the moment decrease more rapidly. Still, no identifiable moment collapse has been obtained. Metallization, defined as overlap of unoccupied with occupied bands, also does not occur until the same range of volume and pressure. However, information from studies of the multiband Hubbard model and comparison of the bandwidth to $U/\sqrt{N}$ ratio ($N=7$ is the $4f$ degeneracy) suggests that a Mott transition might be expected in the broad vicinity of 500 GPa.

The same LDA+U method, and three different correlated band methods have been applied to antiferromagnetic MnO. The manganese configuration is half filled and fully polarized, as is Gd, with the difference being that it is $3d$ and an antiferromagnetic insulator rather than $4f$ in a background of itinerant bands. All methods obtained a volume collapse from a high-spin to low-spin configuration. Surprisingly, the collapse was not to nonmagnetic but rather to a spin-half result.

The critical pressures for transitions suggested by the present study (minimum of 200 GPa, more likely around 750 GPa) lie well above the volume collapse transition that is observed at 59 GPa. At this point in our understanding of the $4f$ shell in Gd, there seems to be no viable alternative to the suggestion by Maddox *et al.* that Gd provides an example of the Kondo volume collapse mechanism.[8]

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