PHYSICAL REVIEW B VOLUME 50, NUMBER 3 15 JULY 1994-I

Elimination of local-spin-density-approximation errors from electronic-structure calculations of Gd

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(Received 17 January 1994; revised manuscript received 11 April 1994)

All previous electronic-structure calculations of Gd have obtained a density of states $N(E_F)$ much larger than the experimental value. By comparing Hartree-Fock with local-spin-density-approximation (LSDA) *atomic* calculations we previously concluded that the minority-spin $4f$ resonance just above E_F in the metal, which is responsible for the enhanced $N(E_F)$, is an artifact of the LSDA. We present here a calculation for the Gd crystal in which the conduction electrons experience a Hartree-Fock potential due to the core electrons and a LSDA potential due to themselves. The resonance is gone, $N(E_F)$ is less than the experimental value (many-body effects will increase it), and the lattice constants are in near-perfect agreement with experiment.

I. INTRODUCTION

It is amazing that the local-spin-density approximation (LSDA), for exchange and correlation which is based on the free-electron gas, works as well as it does for atoms, molecules, and solids. We[1,2] have recently been discussing two errors in the LSDA exchange potential for valence electrons inside the atomic core. One of these errors is important only for magnetic systems and has not previously been noted because most of its effects are fortuitously canceled by an error in the (LSDA) correlation. The other error, while not small, was not noticed because either it had very little overall effect on valence electrons or, when the effect was large, it was blamed on the LSDA as a whole rather than as a core effect. These errors become obvious in a Taylor series expansion of the exchange potential experienced by any electron with spin σ in the core region where $\rho_{\text{core}\sigma} \gg \rho_{\text{val}\sigma}$. We have (in Ry)

$$V_{x,\sigma}^{\text{LSDA}} = -2(6/\pi)^{1/3}(\rho_{\text{core}\sigma}+\rho_{\text{val}\sigma})^{1/3}$$
$$\approx -2(6/\pi)^{1/3}[\rho_{\text{core}\sigma}^{1/3}+\tfrac{1}{3}(\rho_{\text{val}\sigma}/\rho_{\text{core}\sigma})^{2/3}\rho_{\text{val}\sigma}^{1/3}] \ . \qquad (1)$$

The $\rho_{\text{core}\sigma}^{1/3}$ term represents the exchange potential seen by core electrons due to core electrons but in the LSDA it is seen by valence electrons as well. It is much larger than the actual exchange potential experienced by valence electrons in the core region, if only because of the core self-exchange term that it (approximately) includes. Because, as a rule, orthogonality to core electrons prevents valence electrons from collapsing into the core region, this much too attractive potential in the core region has only a moderate effect on the valence electrons. We showed,[2] however, that the unoccupied $4f$ minority-spin states of the LSDA Gd atom not only have a lower eigenvalue than those of the occupied $5d$ and $6s$ states but also have very corelike eigenfunctions, whereas the $4f$ minority-spin states of the Hartree-Fock (HF) atom are unbound, and even if assumed occupied (by promoting the $5d_\uparrow$ electron into the $4f_\downarrow$) are extremely weakly bound, having an eigenvalue and (outside the core region) an eigenfunction that are almost identical to those of an occupied $5f_\uparrow$ state.

We[2] have noted that all Gd energy-band calculations[3-7] yield densities of states at the Fermi energy $N(E_F)$ which exceed the experimental value[8] and have very narrow resonance bands of minority-spin $4f$ electrons just above E_F. It had been pointed out[3] that at least some of the excess $N(E_F)$ was attributable to hybridization between the minority-spin $4f$ bands and minority-spin conduction bands at E_F; we suggested that the minority $4f$ resonance bands are an artifact of the overly attractive minority-spin LSDA exchange potential for unoccupied states in the core region, and that with a better exchange potential they would not exist and the calculated $N(E_F)$ might be consistent with experiment. In this paper we show that that is the case.

The second term in Eq. (1) represents the exchange potential between valence electrons and is unphysically reduced by a factor of $\frac{1}{3}(\rho_{\text{val}}/\rho_{\text{core}})^{2/3}$. This reduction is normally welcome since it partially compensates for the large error in the first term. However, if the valence electrons are spin polarized, this factor gives a huge unphysical reduction in the polarization energy of the valence electrons in the core region. For d electrons, whose wave functions peak quite close to where those of the outermost core electrons peak, this can be a very large effect. Because the LSDA usually yields approximately the correct magnetization, there must exist a canceling error. Since the LSDA for correlation does not apply to rapidly varying charge densities nearly as well as the LSDA for exchange does, we suspect the correlation functional does not adequately represent the screening of the exchange potential due to correlation. This cancellation is good but not complete. Although the LSDA yields good values for the magnetization of Fe, Co, and Ni, it underestimates their magnetic energy, as demonstrated by the fact that[9] it yields the correct bulk modulus for all $3d$ and $4d$ transition metals except Fe, Co, and Ni and that it finds paramagnetic face-centered-cubic Fe to be the ground state.[10] We[1] recently calculated the properties of

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a nine-layer Rh(001) film where the valence electrons experienced a HF core potential and a LSDA potential among themselves but without correcting the screening of the exchange potential. We found the surface of Rh(001) to be ferromagnetic. This engendered a Comment[11] that the LSDA yields the Fe magnetization and Rh magnetic susceptibility in agreement with experiment, whereas our potential makes both of these much too large, and that since the LSDA does not yield Rh surface magnetization, our prediction was incorrect. We[12] were in general agreement with these comments but pointed out that there is some experimental evidence[13] that the Rh(001) surface is ferromagnetic. If this experimental result should hold up, perhaps the reason the HF-core/unscreened-LSDA-valence potential yields the correct result is that surface screening is weaker than bulk screening. In cases such as surfaces or magnetic $4f$ cores, there is no straightforward *ab initio* way to screen the LSDA exchange interaction. The ordinary LSDA with its canceling errors yields[3–7] quite reasonable values for the magnetization of Gd; however, to eliminate the excessively attractive $\rho_{\text{core}}^{1/3}$ term which causes the unoccupied minority $4f$ state to collapse into the core (in the atom) or become a low-lying resonance (in the crystal), we must use the HF-core/LSDA-valence exchange potential, screening the crystal valence exchange potential in an *ad hoc* manner with a single adjustable parameter. The test of this procedure will be comparison of our results with experiment.

II. COMPUTATIONAL PROCEDURES

Using the spin-orbit-averaged Dirac equation[14] we performed a HF calculation[15] for a Gd atom in the $4f_\uparrow^7 5d_\uparrow 6s^2$ configuration (fractional occupancy is not possible for HF calculations). Then those core electrons, taken to be rigid, were used in a spin-orbit-averaged Dirac calculation in which the valence electrons experience a HF exchange potential from the core electrons and a LSDA potential amongst themselves, with the Gd atom in a $4f_\uparrow^7 5d_\uparrow^{0.82} 5d_\downarrow^{0.18} 6s^2$ configuration, corresponding to the crystal spin polarization. The LSDA potential contains von Barth–Hedin[16] (vBH) correlation with Hedin-Lundqvist[17] (HL) parameters. The majority-spin $4f$ electrons are treated as core electrons, since in the HF calculation[2] they lie over 17 eV below the lowest-lying valence electrons[18] and their wave functions are exceedingly corelike.

Combining the Troullier-Martins[19] method for maximum smoothness and that of Rappe *et al.*[20] for minimization of the large wave-vector content, we constructed ionic pseudopotentials for the $5d_\uparrow$, $5d_\downarrow$, $6s_\uparrow$, $6s_\downarrow$, $6p_\uparrow$, and $6p_\downarrow$ eigenstates as well as for unbound[21] $4f_\downarrow$ and $5f_\uparrow$ states. The d pseudopotentials have a cutoff radius of 2.5 bohrs and the others have $r_c=2.8$ bohrs. The HF core exchange tails were cut off at an approximate Wigner-Seitz radius of 3.746 bohrs. The usual factorized form[22] was used for all except the $4f_\downarrow$ where a comparison of the energy dependence of the phase shifts of the wave function with the pseudo wave function was unsatisfactory. This was corrected by calculating the pseudopotentials for unbound $4f_\downarrow$ functions at two energies, 0 and -0.6 Ry, and combining them with the norm-conserving Vanderbilt procedure.[23,24] Figure 1 displays the minority-spin pseudopotentials; the majority-spin pseudopotentials differ only slightly.

We use the following exchange-energy functional in the crystal:

$$E_x[\rho_\uparrow,\rho_\downarrow]=-3(3/4\pi)^{1/3}\{(1-\gamma)(\rho_\uparrow^{4/3}+\rho_\downarrow^{4/3}) +2^{-1/3}\gamma(\rho_\uparrow+\rho_\downarrow)^{4/3}\}\ , \tag{2}$$

where γ is a parameter that will be chosen to obtain the correct magnetization. Here, of course, ρ_σ represents the valence charge density since the HF core exchange is included in the spin-dependent pseudopotentials. Note that Eq. (2) reduces the energy gained by polarizing the crystal but not the exchange energy of the unpolarized crystal. The longer wave-vector components of the difference between the majority and minority HF core potentials should, in principle, also be screened. Since there is no practical way to do this, its effect will be compensated for by γ taking a larger value than a strictly valence polarization screening would demand. In cases where there is no core polarization, a somewhat more physical form of valence polarization screening might be considered,

$$E_x[\rho_\uparrow,\rho_\downarrow]=E_{sx}[\rho_\uparrow]+E_{sx}[\rho_\downarrow]+E_x[\rho]-E_{sx}[\rho]\ , \tag{3}$$

where $E_{sx}[\rho_\sigma]$ and $E_{sx}[\rho]$ are the screened LSDA and screened LDA (Ref. 25) exchange density functionals. These functionals contain a screening wave vector which can either be treated as a parameter or taken to be the Thomas-Fermi wave vector[26] $K_{\text{TF}}=2(k_F/\pi)^{1/2}$. Perdew[27] finds that the LSDA overestimates the correlation energy between parallel-spin electrons in atoms. Presum-

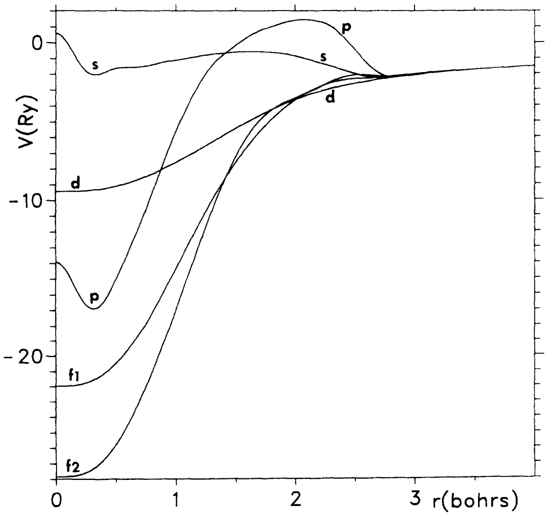

FIG. 1. Gd minority-spin pseudopotentials calculated at the atomic eigenvalues except for the unbound f functions whose pseudopotentials were calculated at -0.6 Ry (f_1) and 0 Ry (f_2).

ably this is also the case for non-free-electron-like states in crystals. Thus the reduction in the exchange energy of the polarized crystal given by Eq. (2) or (3) compensates for this failure of the LSDA to adequately reduce the correlation energy of the polarized crystal. However, because correlation, unlike exchange, depends on unoccupied states, it differs markedly from system to system. Therefore we believe it will be very difficult to obtain an unparametrized exchange-correlation functional which is adequate for all spin-polarized systems.

Using Eq. (2) for exchange and vBH-HL correlation[16,17] we performed electronic-structure calculations for Gd. The hexagonal-close-packed Brillouin zone (BZ) was sampled at 1928 points, which is 108 points in its $\frac{1}{24}$th irreducible wedge consisting of four hexagonal planes at $(2\pi/c)$ $(\frac{1}{16}, \frac{3}{16}, \frac{5}{16}$, and $\frac{7}{16})$. There are two ways to choose the hexagonal array of points. One minimizes the (triangular) proximity area associated with each point sampled. The one we chose minimizes the distance from the sample point to the farthest point on the perimeter of its (hexagonal) proximity area. Using our[28] conjugate gradient method we expanded the wave functions in all plane waves with kinetic energy <50 Ry (between 2646 and 2689 plane waves at the various BZ points for the equilibrium lattice) to obtain the results presented in Sec. III. Although we did not test convergence in the crystal, we expanded the atomic wave functions[29] in spherical Bessel functions, finding that the $p_\uparrow$ and $p_\downarrow$ eigenvalues for $k^2_{\max}=50$ Ry were within 16 and 44 μRy of convergence, respectively, whereas all the f, d, and s eigenvalues were converged to better than 5 μRy.

III. RESULTS

With $\gamma=0.688$ we obtained a spin magnetization of 7.633 μ_B/atom, essentially identical with the experimental value,[30] which contains both spin and orbital components. Although it has been stated[3,5] that adding an orbital component to the calculated magnetization will increase it by between 0.04 and 0.05 μ_B/atom, that is an artifact of the fictitious minority 4f resonance. The orbital component reduces the magnetization of states just below E_F; if those are predominantly minority-spin states, it increases the net magnetization. For the current calculation we expect the effect to be small and cannot even predict its sign. In Table I all our results are compared with the recent calculation of Singh[3] and with experiment. In Fig. 2 the minority and majority spin, as well as the total densities of states $N(E)$, are displayed. Our $N(E_F)=18.57$ states/atom Ry is sufficiently far below the experimental value[8] to account for the many-body corrections whereas, depending how far their resonant minority f bands lay above E_F, other workers obtained between 25 and 47 states/atom Ry.[3–7]

TABLE I. Lattice constants, elastic stiffness constants, bulk modulus, density of states at the Fermi energy, fcc and hcp energy difference, cohesive energy, and magnetization of Gd compared with Singh's calculated values and experiment. Those values in parentheses represent our fit to Singh's data. Note that the BK calculation contains a single parameter γ, which was chosen to obtain the experimental value of M.

	BK	Singh	Expt.
c (bohr)	10.897	(10.596) 10.594	10.902[a]
a (bohr)	6.873	(6.614) 6.617	6.858[a]
$(c_{11}+c_{12})$ (GPa)	93.63	(91.04)	108.25[b]
c_{33} (GPa)	78.81	(78.37)	78.99[b]
$\frac{1}{2}(c_{31}+c_{13})$ (GPa)	19.14	(19.70)	19.10[b]
B (GPa)	38.05	(37.63) 38.8	41.2[b]
$N(E_F)$ (Ry atom)$^{-1}$	>18.57	>27.1	21.35[c]
E (fcc-hcp) (mRy/atom)	1.5	0.9	>0
$E_{\rm coh}$ (eV/atom)	4.344		4.14[d]
M (μ_B)	7.6328	7.57	7.63[e]

[a] Reference 32.
[b] Reference 34.
[c] Reference 8.
[d] Reference 31.
[e] Reference 30.

That our calculated cohesive energy exceeds the experimental value[31] by 5% is typical for transition metals. That our c lattice constant, calculated at 0 K, agrees so well with the experimental one,[32] measured at 106 K, is pure coincidence. Nevertheless, the agreement between calculated and experimental lattice constants is spectacular. We calculated the elastic constants c_{33} and c_{13} from calculated stresses when $\pm2\%$ strains were applied along the c axis and $(c_{11}+c_{12})$ and c_{31} when $\pm1\%$ strains were applied along the a axes. The average[33] of $c_{13}=19.06$ and $c_{31}=19.22$ GPa is given in Table I. The experimental values[34] are obtained from speed of sound measurements at 0 K where adiabatic and isothermal elastic constants should be identical. We do not understand the relatively poor agreement between calculated and experimental values for $(c_{11}+c_{12})$ when c_{33} and c_{13} and the lat-

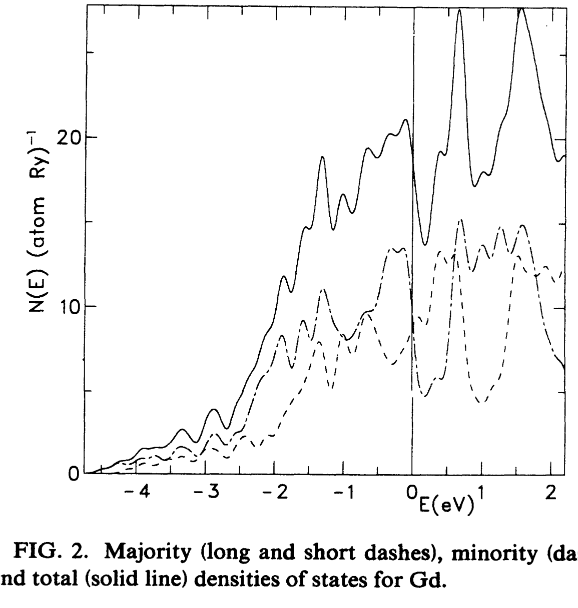

FIG. 2. Majority (long and short dashes), minority (dashes), and total (solid line) densities of states for Gd.

tice constants agree so well, although the experimental c_{12} may be somewhat less accurate than the others since it is the only one that could not be measured in the absence of a magnetic field. The energy of the fcc crystal was calculated with a 6912-point BZ sample (182 in the $\frac{1}{48}$th irreducible wedge). Since the energy tends to drop with denser BZ sampling and since the fcc sampling is 79% denser than the hcp, the sign of the fcc-hcp energy difference in Table I is believed to be correct, although the magnitude may not be completely converged with respect to BZ sample size. Singh[3] calculated the bulk modulus by fitting 25 calculated energies with a polynomial in (c/a) and Ω, the unit-cell volume. He kindly sent us his data which we refitted with a polynomial in c and a, obtaining the elastic constants shown in Table I. We calculated bulk moduli from

$$B=\frac{c_{33}(c_{11}+c_{12})-2c_{13}^2}{(c_{11}+c_{12})-4c_{13}+2c_{33}} \; . \tag{4}$$

The discrepancy between Singh's direct fit of B and our value for his B obtained from (4) and a fit of the c_{ij} is a little larger than one might have hoped.

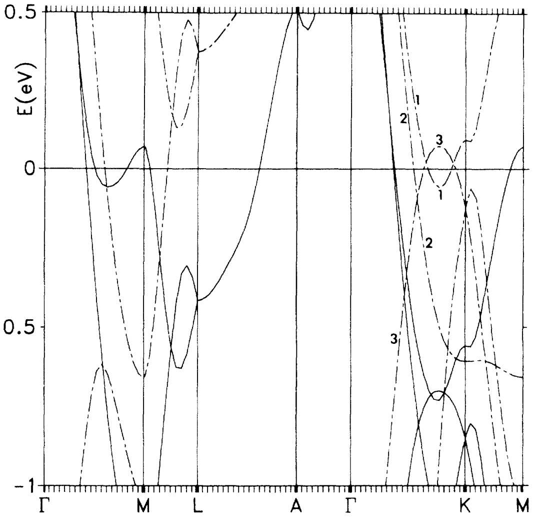

FIG. 4. Energy bands of Gd near the Fermi energy. Three minority-spin bands discussed in the text are labeled.

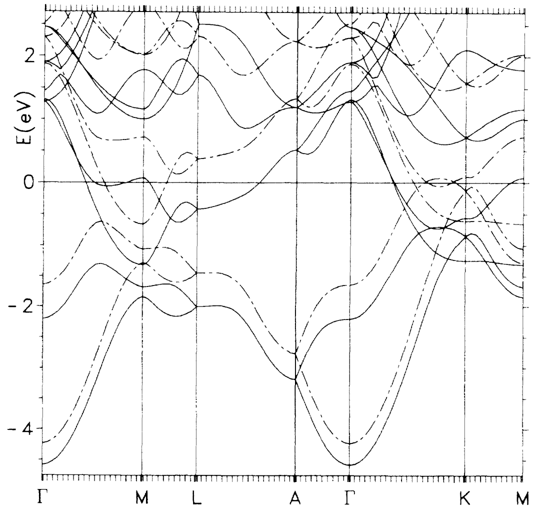

FIG. 3. Energy bands of hcp Gd. The solid lines represent majority-spin states and the dashed lines are the minority spins.

The Gd energy bands are displayed in Fig. 3 and an expanded version around E_F in Fig. 4. A much smaller exchange splitting of the d bands is required to get the correct magnetization than in previous calculations because of the absence of the large minority f-band hybridization below E_F. The lowest states at Γ which are s-like with a small $d_{3z^2-r^2}$ component are split by 0.352 eV and the next states which are mainly $d_{3z^2-r^2}$ with a small s component are split by 0.552 eV. Singh's values for these splittings are 0.90 and 0.97 eV. The experimental value[35] for the upper splitting is ~0.8 eV but the minority-spin photoemission peak is so broad that this value must be considered somewhat uncertain. Furthermore, there can be large self-energy corrections to d-electron excitation energies which reduce the measured splitting relative to the band splitting. Although our calculation allows for both majority- and minority-spin f-electron hybridization into the energy bands, we do not have the complexity introduced by the minority $4f$ resonance just above E_F. Singh[3] states that without this complexity one cannot account for the two small pieces of Fermi surface observed in de Haas–van Alphen measurements.[36] In fact, our bands have the same small hole piece centered at M as do his. Our structure at the K point is markedly different; in particular, our bands do not have Singh's hole piece of Fermi surface centered at K. However, along the T line (from Γ to K) there are two minority-spin bands, T_3 and T_1, which cross each other twice just above E_F. The spin-orbit interaction will open gaps at those crossings. If the Fermi energy lies in the gap, there will be no pieces of Fermi surface there (although there might be elsewhere in the vertical BZ reflection plane off the T line); if E_F lies below the gap, two very tiny hole pieces would be there. More likely, however, the second observed piece of Fermi surface is the electron piece formed by the spin-orbit gap at the T_3-T_2 crossing below E_F. Very recently Ormeci, Wills, and Albers[37] have performed *fully* relativistic calculations of the Gd Fermi surface both with and without $4f$ hybridization. Both calculations were consistent with experiment, indicating that, at least until de Haas–van Alphen data are able to determine where the two Fermi surface pieces are in the Brillouin zone and whether they are electron or hole pieces, they will not be of much help in determining whether the minority-spin f bands are strongly hybridized at E_F.

In conclusion, we previously asserted[2] from a comparison of HF and LSDA atomic calculations that the minority-spin $4f$ resonance bands present in all LSDA band calculations are an artifact of the LSDA. This calculation contains all f contributions, but because it uses a HF core potential, does not have the $4f$ minority resonance. We believe that a comparison of previously and presently calculated lattice constants, elastic constants, and Fermi surface densities of states with experiment represents convincing proof that this assertion is correct.

After this work was completed we became aware of inverse photoemission data[38] which indicate a minority-spin $4f$ resonance about 4.3 eV above E_F. We therefore extended our energy range at Γ to 10 eV above E_F. We find no clustering of minority-spin f bands which begin at 8.36 eV, and of the fourteen $4f_\downarrow$ states at Γ (because there are two atoms per unit cell) no more than six are below 10 eV. This discrepancy with experiment may be an artifact of using a plane-wave expansion and pseudopotentials. Although our pseudopotential cutoff radius is fairly short range, it is not short range with respect to a $4f$ core function. If one looks at the $4f_\downarrow$ function in Fig. 3 of Ref. 2, one sees that it starts out like a core function but as it approaches the axis it bends around and extends outward for over 30 bohrs. It costs kinetic energy for the wave function to bend like that and, if the boundary condition were that it came in flat at the Wigner-Seitz radius rather than at infinity, it might well collapse back into the core. Thus with our exchange-correlation potential, an all-electron calculation might agree with the inverse photoemission data. In either event, whether the $4f_\downarrow$ are corelike functions 4.3 eV above E_F or extended functions more than 8.3 eV above E_F, their hybridization with states at and below E_F is quite small.

Also after this work was completed, Heinemann and Temmerman[39] determined that the LSDA ground state of Gd is antiferromagnetic but that with gradient corrections the ground state is ferromagnetic. The gradient corrections do not appear to have reduced the minority-spin $4f$ contribution below E_F in this atomic-sphere calculation. Therefore, using the same ionic pseudopotentials and same valence exchange [i.e., Eq. (2) with the same value of γ] and correlation functionals we calculated the antiferromagnetic state. Not only does it lie 118 meV/atom above the ferromagnetic ground state, but its equilibrium lattice constants, $c=10.749$ and $a=6.903$ bohrs, are in poorer agreement with experiment. Thus our modified exchange-correlation potential corrects two results of a LSDA calculation of bulk Gd, its magnetic ground state and its density of states at the Fermi surface.

ACKNOWLEDGMENTS

This work was supported by Cray Research, Inc., the University of Texas Center for High Performance Computing, the Welch Foundation (Houston, TX), and the National Science Foundation under Grant No. DMR 9313645.

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the states near E_F. We made a crude approximation for this correction without which $c_{13}=c_{31}=19.06$ GPa.

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