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# Magnetic transitions in bcc vanadium, chromium, manganese, and iron

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We have examined the transition from nonmagnetic to ferromagnetic behavior for elemental bcc vanadium, chromium, manganese, and iron by analyzing self-consistent parameter-free total-energy band-structure calculations in the local-spin-density approximation utilizing a fixed-spin-moment procedure. All systems are found to exhibit singular behavior and to undergo complex transitions as a function of volume. For each system, we find a set of critical Wigner-Seitz radii $r_{\text{WS}}$ defining the onset of magnetic behavior and the end of nonmagnetic behavior. Vanadium and manganese exhibit composite (second-order and first-order) transitions with nonmagnetic low-spin and high-spin magnetic behavior. Chromium undergoes a first-order transition from nonmagnetic to magnetic behavior at expanded volumes, and iron undergoes a second-order transition and becomes nonmagnetic at reduced volumes.

## INTRODUCTION

In transition metals, with partially occupied $d$ bands, it is often possible to lower the total energy by imposing a spin splitting between the up- and down-spin density of states. Since the density of states implicitly depends on the volume of the system, different spin splittings, accomplished by transferring electrons from one spin direction to another, can be energetically favored at different volumes. In general, transition metals will favor a magnetic state at large volumes, where the density of states tends to exhibit peaks, and a nonmagnetic state at low volumes, where the density of states becomes smeared in energy. Thus, any of a number of different magnetic states can be favored, depending upon the detailed location of the Fermi energy in the up- and down-spin density of states. Since different magnetic states are favored in different volume ranges, we expect normally occurring nonmagnetic transition metals to become magnetic at expanded volumes and normally occurring magnetic transition metals to become nonmagnetic at reduced volumes. As a function of volume, we expect a given system to undergo a transition from one state to another.

All of our work on magnetic transitions is based on two features of our calculations. We utilize (1) a fast augmented-spherical-wave procedure which permits self-consistent total energy calculations, and (2) a fixed-spin-moment[1] procedure which finds total energies as a function of both volume and magnetic moment as independent variables. These procedures are essential for studying transition regions where the total energy versus magnetic moment can exhibit more than one minimum. Conventional spin-polarized band calculations are not easily utilized in these volume ranges because of convergence difficulties, and because only one solution (i.e., one energy minimum) is possible for a given starting potential.

For a given volume (Wigner-Seitz radius), we calculate the total energy versus magnetic moment, $E(M)$ curve. We find $E(M)$ curves with local minima at $M=0$ for volumes at which a given system is nonmagnetic, and $E(M)$ curves with local minima at finite $M$ values for volumes at which the system is magnetic. Our conclusions on magnetic transitions are based on studies of $E(M)$ curves for Wigner-Seitz radii spanning the transition region. In contrast with the work of others, we show that the volume dependence of the magnetic moment is necessarily singular, and is usually multivalued and discontinuous.[2] We show that different states terminate at well-defined critical $r_{\text{WS}}$ values, and classify different transitions as type I, type II, type III, etc., depending upon the number of singularities or critical $r_{\text{WS}}$ values (one, two, three, etc.) displayed. We find,[2,3] for example, that bcc Ni, fcc Co, bcc V, and fcc Fe undergo type I, type II, type III, and type IV transitions, respectively. In addition, preliminary results[4] for bcc Mn and fcc Pd imply that these systems undergo type III and type I transitions, respectively. In the present study, we present detailed results for the bcc sequence V, Cr, Mn, and Fe, and show that bcc iron undergoes a transition to the nonmagnetic state under compression.

## MAGNETIC TRANSITIONS

### Vanadium

The volume dependence of the magnetic behavior of bcc vanadium was studied as early as 1973 by Hattox *et al.*[5] This work, based on conventional spin-polarized energy-band calculations (i.e., floating moment), found that bcc vanadium is magnetic at expanded volumes and also showed the existence of two distinct self-consistent solutions at a lattice constant of 7.0 a.u. ($r_{WS}=3.45$ a.u.). The two solutions, found by using two different starting potentials corresponding to different starting magnetic moments, were correctly identified as resulting from a double minimum in the energy versus moment curve for this particular lattice constant. They found the system to be nonmagnetic below $r_{WS}=3.10$ a.u., and magnetic at $r_{WS}\geq 3.45$ a.u. For the region between $r_{WS}=3.10$ and 3.45 a.u., however, they were apparently unable to obtain converged solutions using conventional spin-polarized band calculations, and consequently did not find the structure of the transition.

We have already shown[2] that bcc vanadium undergoes a type III transition at a large lattice expansion. Our calculated total energies and magnetic moments for this system are shown in Fig. 1 where we clearly see the existence of a nonmagnetic (NM), a low-spin (LS), and a high-spin (HS) state. Here, the energy minimum occurs at $r_{WS}=2.79$ a.u. where the system is nonmagnetic, in

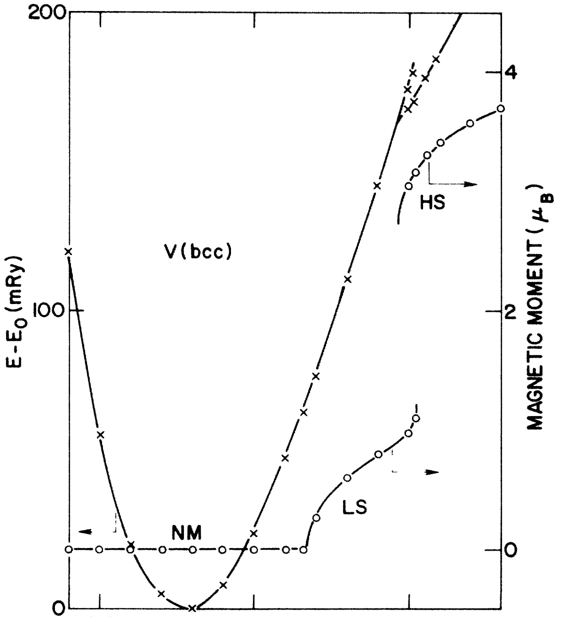

FIG. 1. Calculated magnetic moment and total energy as a function of $r_{WS}$ for bcc vanadium, showing a type III transition and the clear existence of a nonmagnetic (NM), a low-spin (LS), and a high-spin (HS) state. This transition is a composite of a second-order transition from a nonmagnetic to a low-spin state, and a first-order transition from a low- to a high-spin state.

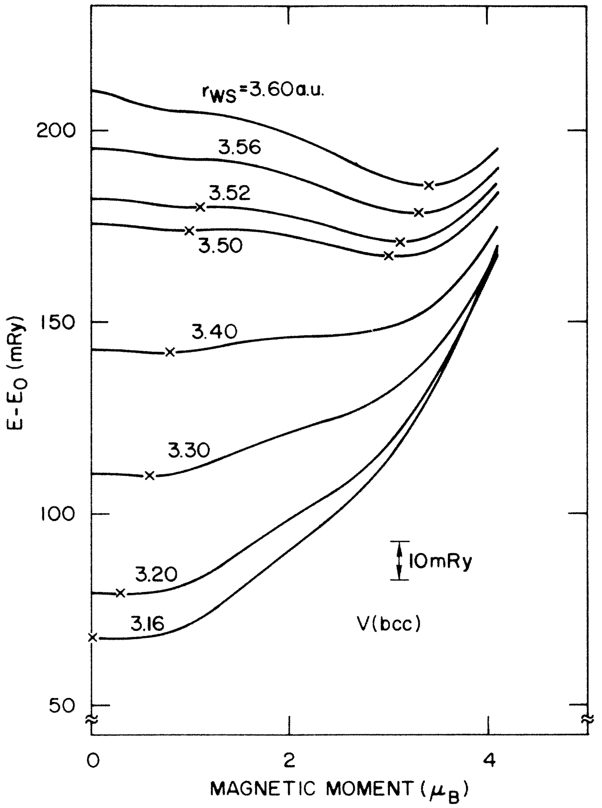

FIG. 2. Calculated total energies as a function of magnetic moment for bcc vanadium at selected values of $r_{WS}$. Local minima marked by × indicate the stable solutions shown in Fig. 1 in the transition region.

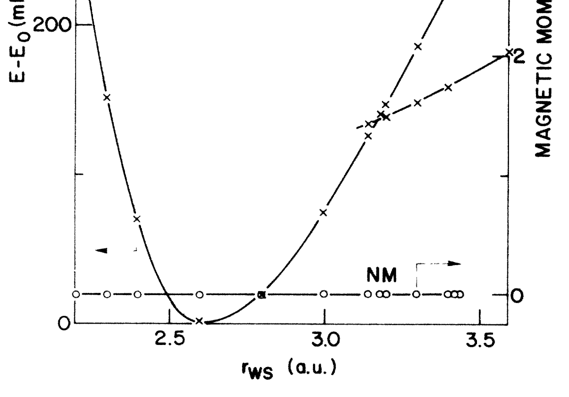

FIG. 3. Calculated magnetic moment and total energy as a function of $r_{WS}$ for bcc chromium, showing a type II first-order transition and the absence of a low-spin state.

agreement with experiment. The three critical $r_{\mathrm{WS}}$ values are 3.17, 3.53, and 3.47 a.u. We note that for $3.47 \le r_{\mathrm{WS}} \le 3.53$ a.u., bcc vanadium can be in either the low-spin or the high-spin state and that it can be driven from one state to the other by applying a magnetic field. The results shown in Fig. 1 are derived directly from calculated $E(M)$ curves like those shown in Fig. 2, which show the existence of a low-spin ($M > 0$) minimum beginning at $r_{\mathrm{WS}} \simeq 3.17$ a.u. and persisting up to $r_{\mathrm{WS}} \simeq 3.53$ a.u. A high-spin solution which is absent for $r_{\mathrm{WS}} = 3.40$ a.u., and just visible at $r_{\mathrm{WS}} = 3.50$ a.u. actually begins at $r_{\mathrm{WS}} \simeq 3.47$ a.u., and continues to higher $r_{\mathrm{WS}}$ values. The beginning of this state at 3.47 a.u. is determined from Fig. 1 and corresponds to the point where the high-spin-state total-energy curve extrapolates to the low-spin-state total-energy curve.[6] The total energies and magnetic moments shown in Fig. 1 represent the loci of the local minima found in calculated $E(M)$ curves like those of Fig. 2. The bulk modulus for this system, obtained from the curvature of total-energy curve at the energy minimum, is 1800 kbars. Note that the transition from the low-spin to the high-spin state occurs near (or slightly beyond) the point of mechanical instability (i.e., the inflection point where the bulk modulus becomes negative).

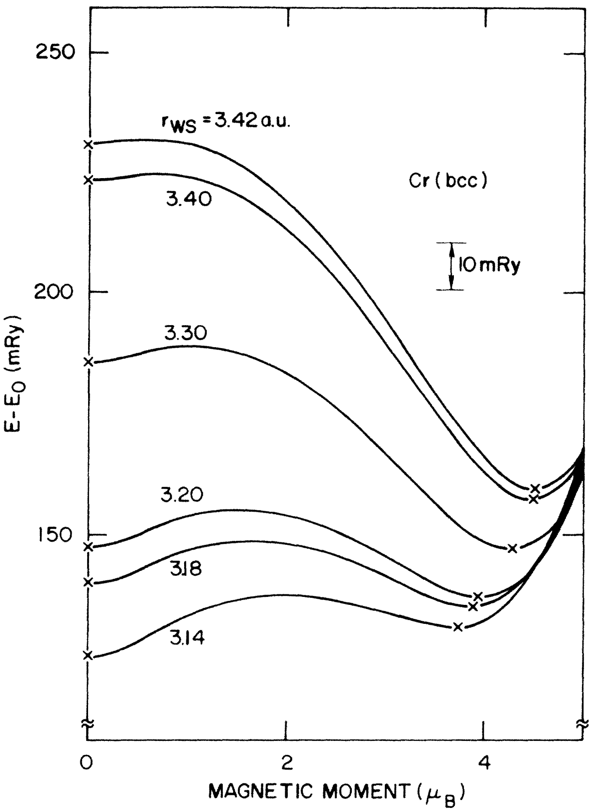

FIG. 4. Calculated total energies as a function of magnetic moment for bcc chromium at selected values of $r_{\mathrm{WS}}$. Local minima marked by × indicate the stable solutions shown in Fig. 3 in the transition region.

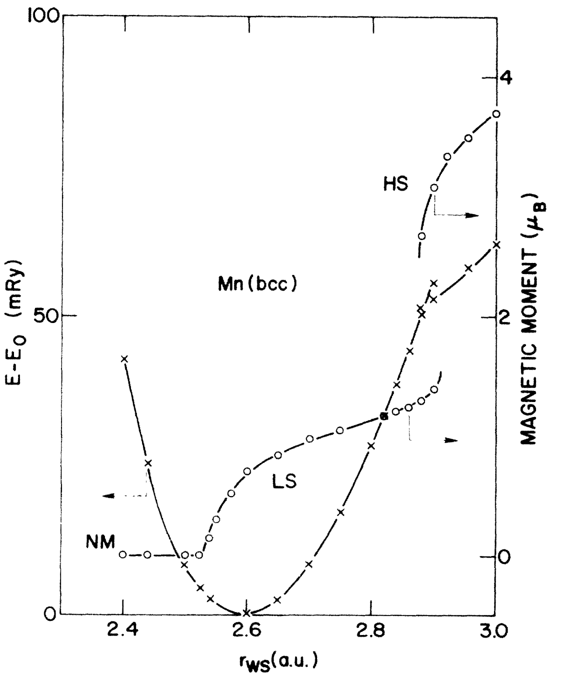

FIG. 5. Calculated magnetic moment and total energy as a function of $r_{\mathrm{WS}}$ for bcc manganese, showing a type III transition similar to bcc vanadium. This transition is a composite of a second-order and a first-order transition.

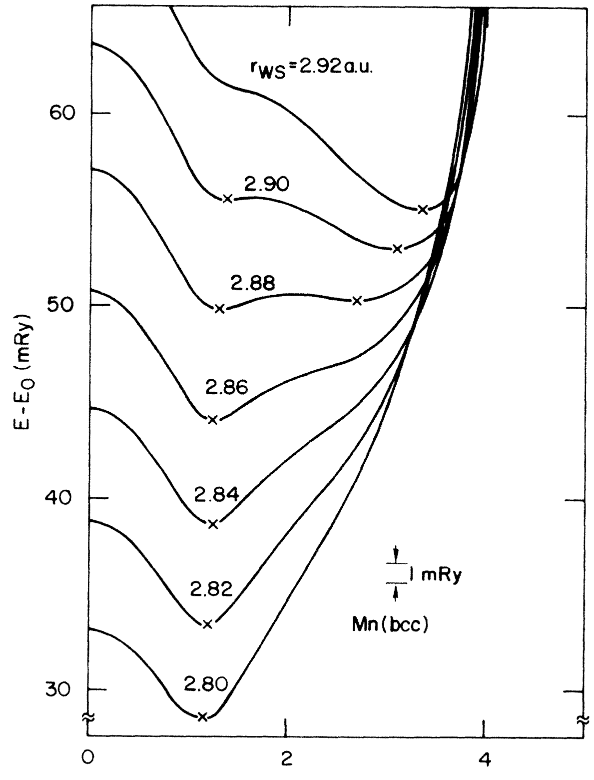

FIG. 6. Calculated total energies as a function of magnetic moment for bcc manganese at selected values of $r_{\mathrm{WS}}$. Local minima marked by × indicate the stable solutions shown in Fig. 5 in the transition region.

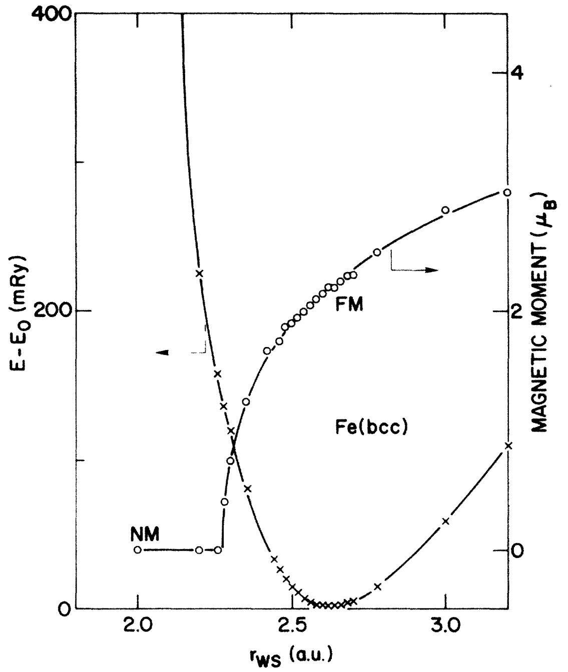

FIG. 7. Calculated magnetic moment and total energy as a function of $r_{WS}$ for bcc iron, showing a type I second-order transition from a nonmagnetic (NM) to a ferromagnetic (FM) state.

## Chromium

Chromium, in the ground state, is an incommensurate antiferromagnet with a bcc structure. Recent[7] band calculations by Kübler and by Skriver, which assumed local moments of nearest-neighbor atoms oriented antiparallel along ⟨001⟩ directions (commensurate antiferromagnetic), yield local moments in good agreement with experiment. In addition, the commensurate antiferromagnetic state is found to have a slightly lower ground-state energy than the nonmagnetic state. Thus, although the true antiferromagnetic state involves spin density waves with a periodicity of many lattice spacings, the commensurate calculations yield reasonable results. In the present work, we do not consider the antiferromagnetic state, but make the assumption that the system is either nonmagnetic or ferromagnetic in order to study the sequence from vanadium to iron.

Constrained to be either nonmagnetic or ferromagnetic, chromium undergoes a type II transition as shown in Fig. 3. As in the case of bcc vanadium, the energy minimum occurs with the system in the nonmagnetic state (at $r_{WS}=2.59$ a.u.) where we find the bulk modulus equals 2700 kbars. Typical $E(M)$ curves for the region where both nonmagnetic and magnetic behavior occur are shown in Fig. 4. In this case, we note the absence of low-spin behavior and the unusually large overlap region where the NM and HS states can coexist.

## Manganese

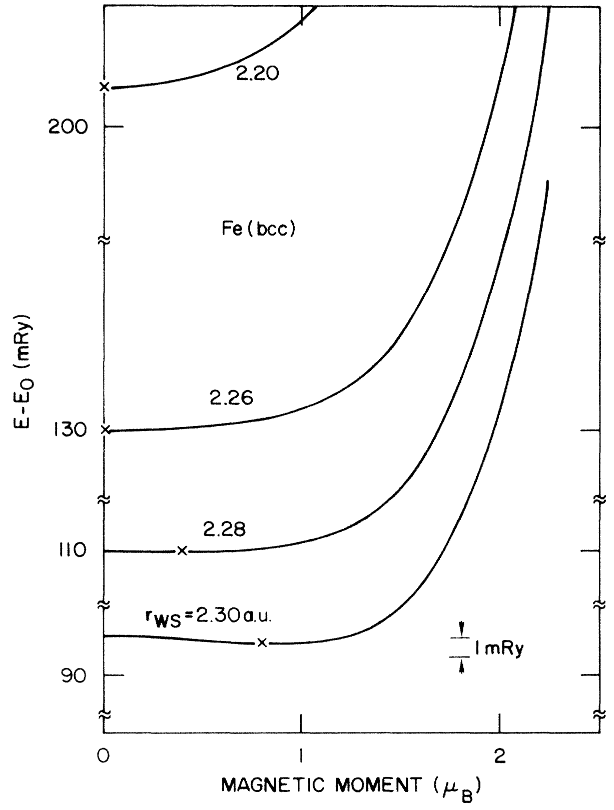

FIG. 8. Calculated total energies as a function of magnetic moment for bcc iron at selected values of $r_{WS}$. Local minima marked by × indicate the stable solutions shown in Fig. 7 in the transition region. Note scale breaks in the energy axis.

Although manganese is stable in the bcc structure only at high temperatures, it has been extensively studied because of its presumed similarity to bcc iron, and because of its proximity to iron in the periodic table. Kübler[8] showed that, constrained to the bcc structure, and assumed to be ferromagnetic, manganese would have a moment of $2.7\mu_B$ at the experimental (high temperature) lattice constant of 5.823 a.u. ($r_{WS}=2.867$ a.u.). In a latter study, Kübler[9] found bcc manganese to prefer the ferromagnetic state from $r_{WS}\simeq 2.55$ to 2.73 a.u. (above 2.73, the antiferromagnetic state is more stable). A more recent study by Fry *et al.*[10] shows that ferromagnetic bcc manganese has a moment ranging from $0.76\mu_B$ to $4.93\mu_B$ in the lattice constant range between 5.20 and 8.00 a.u. ($r_{WS}$ between 2.56 and 3.94 a.u.). This latter work shows an abrupt (steep but continuous) variation of the magnetic moment from $1.26\mu_B$ to $3.12\mu_B$ at a lattice constant of approximately 5.95 a.u. ($r_{WS}\simeq 2.93$ a.u.). This work, based on conventional spin-polarized band calculations, shows the general features but misses the details of the transition.

The present study based on fixed-spin-moment calculations shows bcc manganese to be very similar to vanadium, except that the energy minimum occurs with the system in a low-spin state. The details of the transition are shown in Fig. 5 where we show that this system undergoes a type III transition, and becomes nonmagnetic under compression and undergoes a transition to a high-spin state with expansion to $r_{WS}\simeq 2.9$ a.u. Here, the ground-state bulk modulus is 2600 kbars. Calculated

TABLE I. Equilibrium Wigner-Seitz radii (a.u.), ground states, bulk moduli (kbar), transition types, and critical Wigner-Seitz radii (a.u.) for bcc V, Cr, Mn, and Fe. The NM critical $r_{WS}$ value refers to the termination of NM behavior, and the HS critical value refers to the beginning of HS or FM behavior. Systems which have type III transitions exhibit LS behavior in the region bounded by the indicated LS critical $r_{WS}$ values.

| System | $r_{WS}$ (at minimum) | Ground state | Bulk modulus | Transition type | Critical $r_{WS}$ values NM | LS | HS |
|---|---|---|---|---|---|---|---|
| bcc V | 2.79 | NM | 1800 | III | 3.17 | 3.17,3.53 | 3.47 |
| bcc Cr | 2.59 | NM | 2700 | II | 3.46 | | 3.12 |
| bcc Mn | 2.59 | LS | 2600 | III | 2.53 | 2.53,2.92 | 2.88 |
| bcc Fe | 2.62 | FM | 2200 | I | 2.28 | | 2.28 |

$E(M)$ curves for $r_{WS}$ in the vicinity of the low- and high-spin state coexistence region are shown in Fig. 6.

### Iron

There have been a number of conventional, spin-polarized energy-band calculations for bcc iron near the energy minimum,[11] but no work has been done in the transition region. Under compression, we expect the up-spin and down-spin densities of states to become spread out in energy and to approach a condition where ferromagnetism is no longer preferred. We find that iron undergoes a type I transition from a nonmagnetic (NM) to a ferromagnetic (FM) state at $r_{WS} \simeq 2.28$ a.u. The magnetic moment and total energy as a function of $r_{WS}$ for this system are shown in Fig. 7. Analysis of the total energy curve near the minimum yields a bulk modulus of 2200 kbars. Selected $E(M)$ curves just below and above the transition are shown in Fig. 8.

## DISCUSSION

Table I summarizes the results of this study and shows that transition metals can exhibit a wide range of magnetic properties when examined as a function of volume. The listed critical $r_{WS}$ values define the ranges for the different types of behavior. In all cases, the NM critical value refers to the termination of NM behavior, and the HS critical value refers to the beginning of HS or FM behavior. Vanadium and manganese, which have type III transitions, exhibit LS behavior in the region between the indicated critical $r_{WS}$ values. In the case of iron, the termination of NM behavior coincides with the beginning of HS behavior. Here, the terms high-spin (HS) and ferromagnetic (FM) both refer to magnetic behavior that persists to large volumes. We note that all systems studied have equilibrium Wigner-Seitz radii of $\simeq 2.6$ a.u. and that the critical $r_{WS}$ values generally decrease with increasing atomic number. Thus, vanadium and chromium are normally nonmagnetic (at equilibrium and subject to the constraint that they can only be nonmagnetic or ferromagnetic), but will exhibit magnetic properties at expanded volumes. Manganese and iron are normally magnetic, but will become nonmagnetic at reduced volumes. The results demonstrate an increasing tendency towards magnetism with increasing atomic number.

The type I transition displayed by bcc iron is second-order, as evident from the continuous variation of the magnetic moment versus $r_{WS}$ (discontinuous derivative at the critical $r_{WS}$ value of 2.28 a.u.), and the smooth variation of the total energy. The type II transition for bcc chromium, on the other hand, is first-order because of the discontinuous behavior of the magnetic moment, and the development of a second, distinct, total-energy curve associated with the magnetic state and crossing the total energy curve for the nonmagnetic state.

The type III transitions shown for bcc vanadium and manganese can be considered as composites made up of a second-order transition from nonmagnetic to low-spin behavior, and a first-order transition from low- to high-spin behavior. We note, for example, a smooth variation in the total-energy curves for both systems in the vicinity of the second-order transition, and the development of separate high-spin-state total-energy curves at the first-order transitions where low- and high-spin states can coexist.

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[1] A. R. Williams, V. L. Moruzzi, J. Kübler, and K. Schwarz, Bull. Am. Phys. Soc. **29**, 278 (1984); K. Schwarz and P. Mohn, J. Phys. F **14**, 1129 (1984).

[2] V. L. Moruzzi, Phys. Rev. Lett. **57**, 2211 (1986).

[3] V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986).

[4] P. M. Marcus and V. L. Moruzzi, J. Appl. Phys. (to be published).

[5] T. M. Hattox, J. B. Conklin, Jr., J. C. Slater, and S. B. Trickey, J. Phys. Chem. Solids **34**, 1627 (1973).

[6] It can be shown that the total-energy curve of the high-spin state must persist down to and must meet the total-energy curve of the low-spin state.

[7] J. Kübler, J. Magn. Magn. Mater. **20**, 277 (1980); H. L. Skriver, J. Phys. F **11**, 97 (1981).

[8] J. Kübler, J. Magn. Magn. Mater. **20**, 107 (1979).

[9] J. Kübler (unpublished)

[10] J. L. Fry, Y. Z. Zhao, N. E. Brener, G. Fuster, and J. Callaway, Phys. Rev. B **36**, 868 (1987).

[11] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).