Singular Volume Dependence of Transition-Metal Magnetism

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The transition from nonmagnetic to magnetic behavior in transition-metal ferromagnets is studied by analysis of all possible volume evolutions of the variation of the total energy with magnetic moment. In contrast to a large body of previous work, magnetic transitions are shown to be necessarily singular, and usually multivalued and discontinuous. Self-consistent spin-polarized energy-band calculations for bcc nickel, fcc cobalt, bcc vanadium, and fcc iron are presented as examples supporting and illustrating the general conclusions.

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The presence or absence of magnetism in transition metals is determined by a competition between intra-atomic exchange interactions and interatomic electron motion. Since the interatomic motion depends strongly on the interatomic separation, and because the *d* bands are partially filled, transition metals are necessarily magnetic at sufficiently large volumes (low densities) and necessarily nonmagnetic at sufficiently low volumes (high densities). Thus, a normally magnetic transition metal, like iron, becomes nonmagnetic when compressed. Conversely, a normally nonmagnetic transition metal, like vanadium, becomes magnetic when expanded.[1] The nature of the transition from nonmagnetic to magnetic behavior, however, constitutes a long-standing problem. All previous results[2] indicate that the variation of the magnetic moment with volume, $M(V)$, is smooth and continuous, even in the transition region. Here, I present a general discussion, based on a Landau-type expansion of the total energy in even powers of the magnetic moment, that shows that this variation *cannot* be smooth and continuous. By examining the simplest possible ways that a system can undergo a transition from nonmagnetic to magnetic behavior, I show that $M(V)$ *always* exhibits square-root singularities, and that $M(V)$ is usually multivalued and discontinuous. The general conclusions are both illustrated and supported by the results of new and carefully performed energy-band calculations based on a local-spin-density approximation.[3] The calculated $M(V)$ curves support the general conclusion that, in the transition region, $M(V)$ must exhibit square-root singularities, and that $M(V)$ is usually multivalued and discontinuous.

At a given volume, the possible magnetic states of a system are completely determined by the variation of the total energy with magnetic moment, $E(M)$. Transitions from one state to another are determined by the evolution with volume of these curves. The simplest possible evolution from nonmagnetic to magnetic behavior is schematically shown in the upper-left panel of Fig. 1. At sufficiently low volumes (lowermost curve), $E(M)$ exhibits a minimum at the origin ($M=0$). In this case, d^2E/dM^2 at $M=0$ is positive and the system is nonmagnetic ($M=0$). At sufficiently high volumes (uppermost curve), d^2E/dM^2 at the origin is negative, so that the minimum must occur at finite M (hence the system is magnetic). Therefore, at some intermediate volume, labeled V_C, the second derivative *must* vanish. The system is nonmagnetic for all volumes less than V_C, and magnetic for all volumes greater than V_C. Starting at V_C, the minimum in the $E(M)$ curves moves continuously away from $M=0$ with increasing volume. The dashed curve shows the locus of the minimum as a function of volume. Note that as V approaches V_C from above the magnetic moment decreases to zero. The $M(V)$ behavior corresponding to this simplest evolution is shown in the right-hand portion of the upper panel of Fig. 1. In this case, $M(V)$ consists of two connected branches, one describing nonmagnetic and another describing magnetic behavior.

The volume dependence of the magnetic moment, $M(V)$, in the immediate vicinity of V_C is most easily described by a Landau expansion of the energy in even powers of M with volume-dependent coefficients. Then

$$E-E_0=\alpha(V)M^2+\beta(V)M^4+\ldots,$$

where E_0 is the energy at zero moment. The lowermost $E(M)$ curve in the upper panel of Fig. 1 (low volume and nonmagnetic behavior), where d^2E/dM^2 is positive at $M=0$, corresponds to positive α and β. The uppermost $E(M)$ curve (high volume and magnetic behavior), where d^2E/DM^2 is negative at $M=0$, corresponds to negative α and positive β. With truncation of the Landau expansion at M^4 (which requires a positive β so that M cannot increase without limit), the minimum-energy requirement is

$$dE/dM=2\alpha(V)M+4\beta(V)M^3=0.$$

Therefore, the volume dependence of the moment at the energy minimum is

$$M^2=-\alpha(V)/2\beta(V).$$

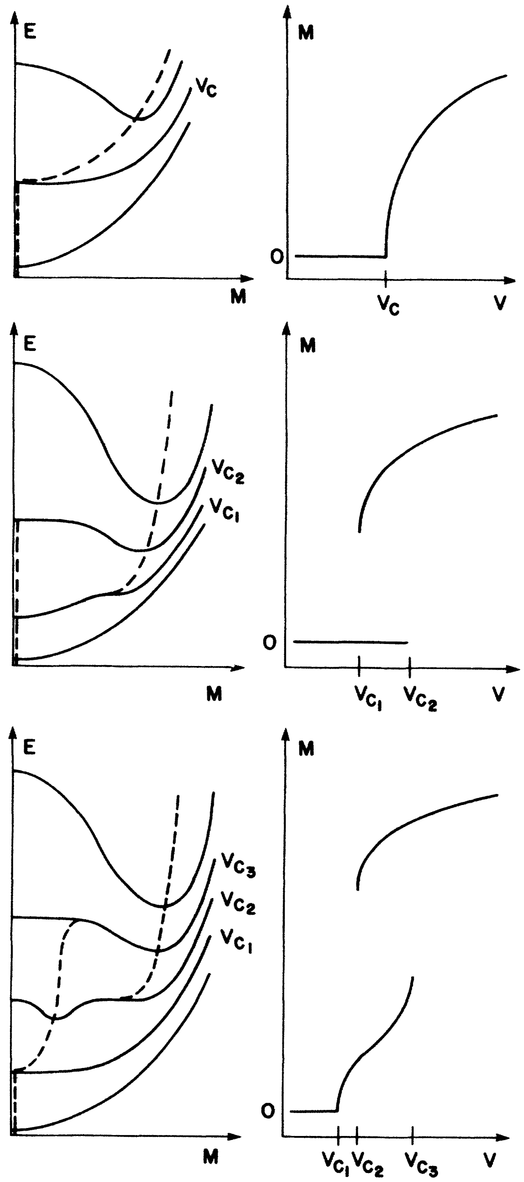

FIG. 1. Schematic representation of the three simplest types of evolution from nonmagnetic to magnetic behavior. The lowermost and uppermost $E(M)$ curves in each left-hand panel correspond to the limiting nonmagnetic (low volume) and magnetic (high volume) behaviors. The dashed curves represent a mapping of the various energy minima. The top, middle, and bottom panels represent type-I, type-II, and type-III transitions, respectively (see text). The expected $M(V)$ behavior is shown by the right-hand panels.

Note that $\alpha(V)$ is a measure of the curvature, d^2E/dM^2 at $M=0$. At $V=V_C$, the curvature changes sign. Therefore, $\alpha(V_C)=0$. In the vicinity of V_C, $\alpha(V)$ is proportional to $V-V_C$, and the equilibrium moment for $V>V_C$ becomes

$$M \propto (V-V_C)^{1/2}.$$

Thus, M exhibits a square-root singularity at $V=V_C$ (with $dM/dV=\infty$), and V_C is a "critical" volume. I classify this simplest evolution exhibiting only one singularity, shown in the top panel of Fig. 1, as a type-I transition.

A more complex behavior occurs if a second minimum develops at finite M. In this case, at some intermediate volume, the system exhibits two local $E(M)$ minima, one at $M=0$ and another at finite M. At this volume the system exhibits the metamagnetic behavior discussed by Wohlfarth and Rhodes[4] and by Shimizu,[4] and can be driven from the nonmagnetic state to the magnetic state by the overcoming of the energy barrier between them (i.e., by application of a magnetic field). This case is shown in the middle panel of Fig. 1. An immediate implication of the existence of two minima at this intermediate volume is the existence of two critical volumes V_{C_1} and V_{C_2} marking the termination of each minimum. For this type of evolution, the magnetic minimum persists for all volumes down to V_{C_1}, where the minimum vanishes at the finite M, and the curvature becomes zero. Likewise, the nonmagnetic minimum persists for all volumes up to V_{C_2}. The corresponding $M(V)$ behavior is shown in the middle-right panel of Fig. 1. The two branches are now separated, and there is an overlapping region where the behavior is discontinuous and multivalued. Since this case exhibits two singularities, the evolution is classified as a type-II transition.

In a type-II transition, the appearance of the second minimum at finite M precludes the onset of a type-I transition (occurs at a lower volume). However, if the second minimum forms at a higher volume than the onset of the type-I transition, the complex evolution shown in the bottom panel of Fig. 1 occurs. At an intermediate volume, the system exhibits two local $E(M)$ minima, both at finite M. As shown in the figure, this evolution implies the existence of three critical volumes. Here the low-volume, nonmagnetic minimum terminates at a third critical volume labeled V_{C_1}, where it joins with the lower termination of the low-moment minimum in the same manner as the type-I transition shown in the top panel. The low-moment minimum must also terminate at a second critical volume labeled V_{C_3} at a finite M value. Furthermore, in this termination, the singularity is approached from below. The high-moment minimum terminates at the critical volume labeled V_{C_2} in the same manner as the type-II transition shown in the middle panel (the location of all minima are shown by dashed lines in the figure). The corresponding $M(V)$ behavior is shown in the bottom panel of Fig. 1. Note the three separate branches and the discontinuity between the high- and low-moment branches. In this case, there are three singularities and the evolution is classified as a type-III transition.

The details of the $E(M)$ behavior in the transition region are system dependent, and can become even more complicated than those shown for type-I, type-II, and type-III transitions. Consider an evolution which involves, at some intermediate volume, an $E(M)$ curve with three local energy minima, one at $M=0$ and two at finite M values. Once again, two magnetic (one at high moments and one at low moments) and one nonmagnetic minima occur, but in this case the branch corresponding to the low-moment minimum does not join with the nonmagnetic branch. The relation of the lower termination of the low-moment branch and the upper termination of the nonmagnetic branch must resemble that exhibited for a type-II transition. Furthermore, the upper termination of the low-moment branch and the lower termination of the high-moment branch must resemble those of a type-III transition. In this case there are four critical volumes, one marking the upper termination of the nonmagnetic minimum, one marking the lower termination of the high-moment minimum and two marking the upper and lower terminations of the low-moment minimum. The $M(V)$ behavior for this case shows a nonmagnetic, a low-moment, and a high-moment branch, similar to that of a type-III transition, but with a discontinuity between the nonmagnetic and the low-moment branch. Evolutions of this kind exhibit four singularities and are classified as type-IV transitions.

Examples of each of the four transition types described above have been identified in the results of first-principles calculations[5] of $E(M)$ curves for bcc nickel,[6,7] fcc cobalt,[6–8] bcc vanadium, and fcc iron.[6] The results are based on electronic structure calculations using the augmented-spherical-wave method of Williams, Kübler, and Gelatt,[9] which assumes the local-spin-density treatment formulated by von Barth and Hedin[10] and modified by Janak.[11] In Fig. 2 I show the calculated M vs V/V_0 behavior. Here V_0 is the calculated equilibrium volume corresponding to zero pressure. The calculated results illustrate that these systems exhibit one, two, three, and four singularities, and undergo type-I, -II, -III, and -IV transitions, respectively. Note that singular behavior occurs at a 1.5% volume expansion for bcc nickel, at approximately a 10% volume compression for fcc cobalt, in the vicinity of a 20% volume expansion for fcc iron, and at a much larger volume expansion for bcc vanadium. The examples shown in Fig. 2 are representative of different possible $E(M)$ evolutions from nonmagnetic to magnetic behavior. Calculations indicate that all transition metals undergo similar transitions. Normally occurring bcc iron and fcc nickel and nonequilibrium bcc cobalt undergo transitions and exhibit singularities at large volume compressions (corresponding to pressures of thousands of kilobars). For fcc vanadium, a

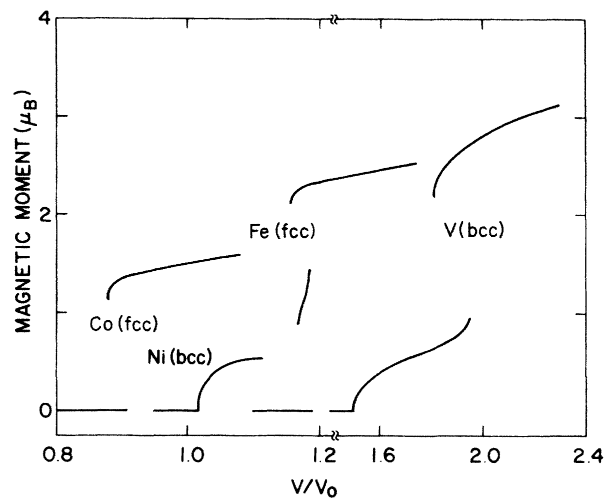

FIG. 2. Calculated $M(V)$ curves for bcc nickel, fcc cobalt, bcc vanadium, and fcc iron showing critical behavior in the transition region. The horizontal axis is the reduced volume, V/V_0, where V_0 is the equilibrium volume. The horizontal scale for vanadium is different from that for iron, cobalt, and nickel. Note that bcc nickel, fcc cobalt, bcc vanadium, and fcc iron exhibit type-I, type-II, type-III, and type-IV transitions, respectively (see text). All results are based on nonrelativistic augmented-spherical-wave electronic structure calculations utilizing a uniform **k** mesh of 507 points for the fcc, and 405 points for the bcc irreducible wedge of the Brillouin zone.

type-I transition is found at approximately the same (expanded) volume as bcc vanadium. A type-I transition is also found for fcc palladium at a small volume expansion, with moments comparable to those of nickel.

Some of the nonequilibrium structures discussed above can be stabilized by clamping thin films at the appropriate lattice constants. Recently, Brodsky and Freeman[12] showed that thin films of palladium sandwiched between thin films of gold, which presumably expanded the lattice constant, exhibited large increases in magnetic susceptibility, and were on the verge of being magnetic. More recently, Prinz[13] demonstrated the feasibility of making thin films of nonequilibrium structures by epitaxial growth on suitably chosen substrates. This rapidly developing capability creates the possibility of artificial stabilization of the structures discussed and of experimental observation of the predicted singular behavior. The bcc-nickel case is particularly appealing for three reasons: (1) The type-I transition is the simplest, (2) the singularity occurs at only a 1.5% volume expansion, and (3) the fcc and bcc equilibrium (zero pressure) volumes are almost the same with a total energy difference at equilibrium of only 4 mRy.[7]

The origin of the singular behavior lies in the details of the single-particle state density which determines the kinetic-energy price required to exploit intra-atomic exchange. The state density is a volume-dependent, mulitpeaked structure dominated by the d bands. At low volumes, the kinetic-energy price is so high that exchange cannot be exploited and a nonmagnetic state is preferred. At high volumes, the kinetic-energy price is low and the system can take advantage of exchange and become magnetic. In principle, there can be a different magnetic state for each major peak in the state density because each controls the kinetic-energy price that must be paid for incremental changes in the magnetic moment. The singularities are the direct result of the appearance and disappearance of different magnetic states.

In summary, I have shown that the transition from nonmagnetic to magnetic behavior must exhibit square-root singularities[14] at critical volumes where dM/dV is infinite, and that $M(V)$ is often multivalued and discontinuous. I have used parameter-free, fixed-moment, spin-polarized energy-band calculations to determine the $M(V)$ behavior for a number of real systems. The results yield a clear resolution of the $M(V)$ behavior in the transition region, and support the general predictions. The major significance of this work is the demonstration that $M(V)$ *cannot* show a gradual decrease to zero moment with decreasing volume. This is a general result that is independent of the method of calculation, and that applies to any system capable of sustaining itinerant-electron magnetic behavior.

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