Giant internal magnetic pressure and compressibility anomalies

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We show that the kinetic-energy increase associated with magnetic ordering is responsible for the anomalously large lattice constants and small bulk moduli of the magnetic members of the $3d$ transition series. The effect follows from the itinerant model of magnetism and does not involve spin-orbit coupling. For Fe and Ni, this effect is demonstrated directly using self-consistent spin-polarized energy-band calculations. A simple, approximate expression for the magnetic pressure is obtained from the Stoner model. This expression gives results for Fe and Ni which are in good agreement with the detailed calculations and is used to obtain estimates of the size of the effect in Cr, Mn, and Co.

I. INTRODUCTION

Changes in the mechanical properties of magnetic metals due to their magnetization are well known.[1] In contrast to those magnetoelastic effects usually attributed to spin-orbit coupling,[2] we consider here the mechanical implication of the kinetic-energy increase due to magnetization[3] and show that it is responsible for the anomalies in the atomic density and bulk modulus of Cr, Mn, Fe, Co, and Ni.[4] These properties are anomalous in the sense that they differ markedly from their $4d$ and $5d$ counterparts and from the trend in the remainder of the $3d$ series. This trend and the very similar $4d$ behavior are accurately described by the results of our earlier nonmagnetic self-consistent energy-band calculations.[5] An interesting aspect of the effect is its magnitude: enormous magnetically derived internal pressures are required to account for the observed atomic volumes of these materials. The mechanism depends on the size of the moment, but probably not crucially on its spatial dependence, and could well be responsible for the polymorphism of Mn.[6]

We were led to this investigation by the results of our systematic application of the nonmagnetic local-density treatment of exchange and correlation to the binding properties of 26 metals in the third and fourth rows of the Periodic Table.[2] The Wigner-Seitz radii[7] and bulk moduli were in excellent agreement with experiment except for the magnetic metals Cr, Mn, Fe, Co, and Ni (see Fig. 1).

Figure 1 shows that, except for these five metals, the measured and calculated Wigner-Seitz radii and bulk moduli exhibit nearly identical parabolic trends with atomic number in both the $3d$ and $4d$ series. The deviation of the Wigner-Seitz radius from this trend for Cr, Mn, Fe, Co, and Ni suggests that some repulsive interaction, present in the real metals, has been left out of the calculations for Cr, Mn, Fe, Co, and Ni. Furthermore, such a repulsive interaction will not only cause the lattice to expand; it will also cause a significant decrease in the bulk modulus B, because dB/da is negative and large in the transition metals (the theoretical bulk modulus is evaluated at the *calculated* equilibrium volume). The fact that these five metals are the only magnetic elements of the 26 considered in Fig. 1 immediately suggests that this repulsive force is a consequence of magnetic ordering.

The forces required to account for the discrepancies in volume are, however, very large (the required internal pressure is estimated to be ~ 460 kbar in Mn, for example)—much too large to be ascribed to spin-orbit effects, which typically involve pressures less than 1 kbar. We have found by direct calculation (self-consistent spin-polarized energy-band calculations) that forces of the required magnitude are, in fact, a consequence of magnetic ordering for Fe and Ni. Because of the more complicated magnetic ordering of Cr and Mn, it would be difficult for us to perform similar calculations for these metals. Nevertheless, a qualitative argument suggests that large magnetic forces are a general consequence of the itinerant model of magnetism, and thus also occur in Cr and Mn. The remainder of this paper is organized as follows: (i) We first show that large magnetic pressures are a general implication of the itinerant model. (ii) We estimate the contribution of this effect to the lattice constant and bulk modulus using the Stoner model. Because of the approximations in the latter, the actual values obtained for the magnetic pressure possess only qualitative significance. Quantitative justification of this particular use of the Stoner model is provided by the fact that the pressures obtained for Fe and Ni are rather close to those obtained from self-consistent energy-band calculations. (iii) Finally, we present some detailed results of our self-consistent calculations for Fe and Ni.

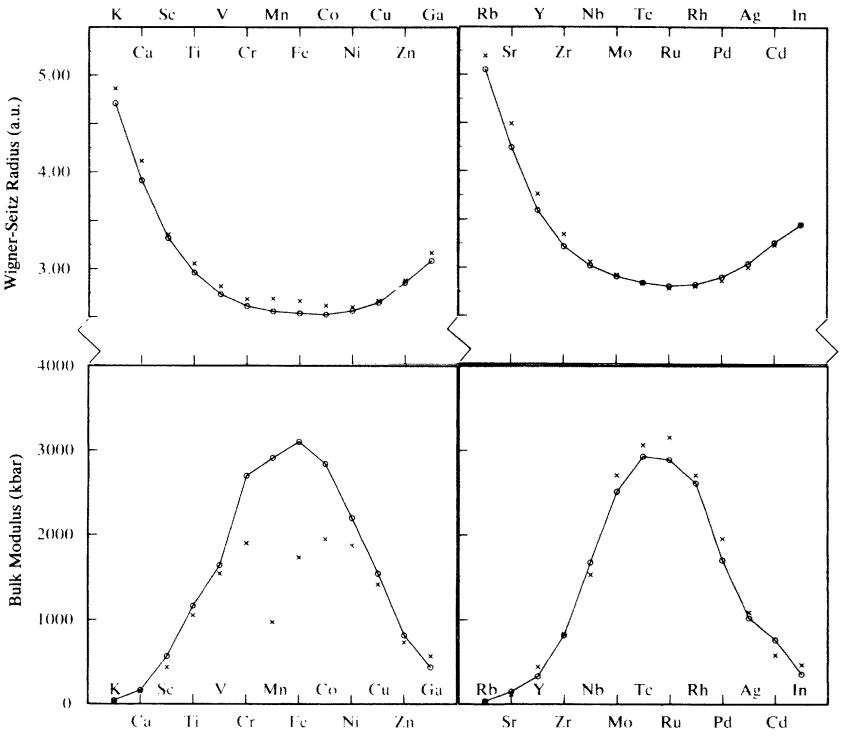

FIG. 1. Equilibrium properties vs atomic number. Top row—equilibrium nuclear separation in terms of Wigner-Seitz radius. Bottom row—bulk modulus in kbar. The atomic number increases in steps of one from 19 to 31 in the left-hand column and from 37 to 49 in the right-hand column. Measured values (low temperature where available) are indicated by crosses (Refs. 4 and 8–15).

II. REPULSION IN THE ITINERANT MODEL

In the itinerant model of magnetism,[16] spin polarization causes a splitting of the bands and an increase in kinetic energy (for small magnetic moments, this kinetic energy increase can be related to the density of states at the Fermi level by the Stoner model[17]). The system orders magnetically when the kinetic energy cost is more than offset by the gain in exchange energy. The repulsive force arises simply because the system can reduce the kinetic energy cost of magnetic ordering by undergoing a lattice expansion.[18]

The detailed mechanism is as follows: the character of the d states changes continuously from low kinetic energy (bonding) at the bottom of the d band to high kinetic energy (antibonding) at the top of the band. When the energy of the majority-spin band is lowered and electrons are transferred into it from the minority-spin band, the result is always a transfer of electrons to higher-kinetic-energy (less bonding) orbitals and thus a net repulsion.

Although this argument is based on ferromagnetic ordering, it also applies to cases where the ordering varies spatially, as for simple antiferromagnets or spin-density waves. As long as it is legitimate to think in terms of a local density of states,[19] the magnetic ordering will still lead to a repulsion, because the effect is independent of which band has its energy lowered. We conclude that, in the itinerant model, magnetic ordering is accompanied by a repulsive force for all values of the magnetic moment, even if the ordering varies spatially.

It remains to establish the magnitude of the repulsion. We have accomplished this for ferromagnetic Fe and Ni by using self-consistent energy-band calculations to find the equation of state. However, these are elaborate computer calculations. In order to obtain estimates of the repulsion for Cr and Mn, where the complicated magnetic ordering makes our self-consistent approach prohibitively expensive at present, we need a simple model which gives results similar to those obtained by direct calculation for Fe and Ni, and which can be easily extrapolated to antiferromagnetic materials. For this purpose, we use the Stoner model,[17] and estimate the repulsion in terms of the pressure obtained from the volume derivative of the lowest term in the expansion of the kinetic-energy increase in powers of the magnetic moment. For simplicity, we neglect the volume dependence of the exchange term,[18] as well as that of all higher terms, even though neither is necessarily small. It should be pointed out that this particular implementation of the above ideas is necessarily much more approximate than the results of self-consistent energy-band calculations. However, the good agreement between magnetic pressures for Fe and Ni obtained from the self-

TABLE I. Parameters for, and results of, the Stoner extrapolation. First column: calculated equilibrium nonmagnetic atomic volume (Ref. 5). Second column: calculated nonmagnetic density of states at the Fermi level (Ref. 5). Third column: measured Bohr magneton number (Ref. 6). Fourth column: Stoner kinetic energy K from Eq. (1). Fifth column: pressure P_M from Eq. (2). Self-consistent spin-polarized calculations give 185 and 8 kbar for P_M in Fe and Ni, respectively.

	Ω (a.u.)	$N(\epsilon_F)$ (Ry^{-1})	$M(\mu_B)$	$K=M^2/2N$ (Ry)	P_M (kbar)
Cr	74.46	10	0.45	0.010	33
Mn	69.78	22	2.4	0.131	460
Fe	68.11	41	2.2	0.059	212
Co	67.13	29	1.7	0.050	182
Ni	70.35	60	0.6	0.003	10

consistent calculations and those obtained in this approximate way suggests that these approximations should be adequate for other materials as well.

The parameters necessary for the Stoner model and the results for Cr, Mn, Fe, Co, and Ni are given in Table I. The paramagnetic densities of states $N(\epsilon_F)$ are those obtained from our nonmagnetic calculations,[5] the magnetic moments M (in Bohr magnetons per atom) are measured values,[6] and the kinetic energy increase K is

$$K=M^2/2N. \tag{1}$$

We also give in Table I the values of the magnetic pressure

$$P_M=-\left(\frac{\partial K}{\partial\Omega}\right)_M=-\tfrac{1}{2}M^2\frac{\partial}{\partial\Omega}\frac{1}{N}\equiv\frac{\lambda K}{\Omega} \tag{2}$$

obtained assuming $\lambda\equiv\partial\ln N/\partial\ln\Omega=\frac{5}{3}$,[20] and the values of the calculated nonmagnetic equilibrium atomic volumes[21] Ω needed in Eq. (2). The values of P_M for Fe and Ni obtained from Eq. (2) (212 and 10 kbar) are remarkably close to those which are found from our full self-consistent spin-polarized energy-band calculations (185 and 8 kbar,[22] respectively); this correspondence lends credence to the Stoner-theory estimates of P_M for the remaining elements in Table I. In Fig. 2, we compare the estimated Wigner-Seitz radius and bulk modulus for the magnetic phases of the five metals[23] with our nonmagnetic calculations[5] and with experiment. The magnetic ordering substantially improves the agreement with experiment.[24] Because of the approximations discussed above, the results of Fig. 2 should not be taken as quantitative. Nevertheless, they certainly indicate the importance of the mechanical effects produced by spin ordering in magnetic materials.

These large changes in atomic volume and bulk modulus cannot be measured directly, because the nonmagnetic phase cannot be prepared at 0 K. However, extrapolations of lattice constants for various magnetic and nonmagnetic alloys to the pure materials[25,26] imply atomic volume changes upon magnetization which are very similar to those shown in Fig. 2 (it follows that these alloys should also show large changes in their elastic moduli as functions of composition). Another indication that repulsive forces exist in antiferromagnets is the negative thermal expansion found in Cr and α-Mn at low temperatures.[27]

Although the changes in bulk modulus or lattice constant shown in Fig. 2 cannot be measured at

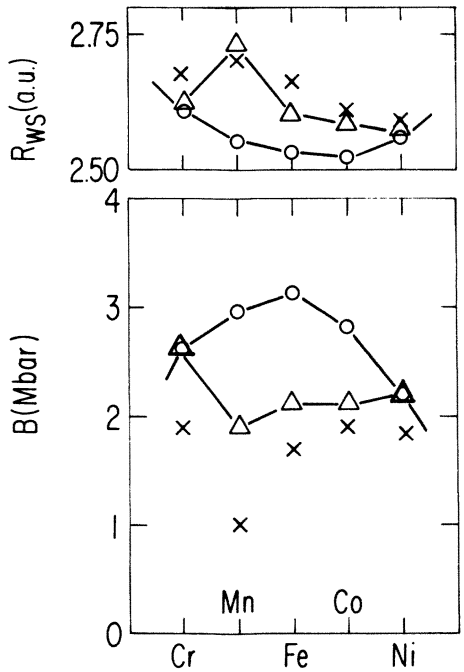

FIG. 2. Wigner-Seitz radius and bulk modulus calculated for nonmagnetic phase (Ref. 5) (circles), and estimated for magnetic phases (triangles) compared to experiment (crosses) (Refs. 4 and 8–15). The scale for the Wigner-Seitz radius is magnified in comparison to Fig. 1.

TABLE II. Calculated cohesive energy, lattice constant, bulk modulus, magnetic moment, and pressure derivative of magnetic moment of nonmagnetic and ferromagnetic bcc Fe compared to experiment.

	E_{coh} (Ry)	a (a.u.)	B (Mbar)	$M(\mu_B)$	$\partial \ln M/\partial P$ (kbar^{-1})
Nonmagnetic	0.442	5.15	3.15	...	...
Ferromagnetic	0.461	5.27	2.17	2.15	-4.9×10^{-4}
Experiment	0.316 [a]	5.40 [b]	1.73 [c]	2.22 [d]	-3.2×10^{-4} [e]

[a] Reference 4.
[b] Reference 9.
[c] Reference 12.
[d] Reference 6.
[e] Reference 38.

absolute zero, they are still quite large compared to the anomalies usually observed at the transition temperature.[10,11,14] One explanation of the difference lies in the possibility of spin fluctuations with long time constants above the ordering temperature, or in persistent local moments.[28] According to the argument given above, either would lead to repulsive forces above the ordering temperature, and the calculated nonmagnetic lattice constant or bulk modulus would still be irrelevant to the actual material.

III. DETAILED CALCULATIONS

Our self-consistent spin-polarized energy-band calculations are similar to our nonmagnetic calculations[5]; we use the muffin-tin approximation, but replace the nonmagnetic exchange-correlation functional of Hedin and Lundqvist[29] by the spin-polarized exchange-correlation functional constructed by von Barth and Hedin.[30-32] There are no adjustable parameters; two energy-band calculations, one for each spin, are performed for each self-consistency iteration, and the magnetic moment per atom is obtained from the difference in the integrated densities of states at the Fermi energy. While there have been several[33-36] self-consistent spin-polarized energy-band calculations for the magnetic $3d$ elements, none were concerned with the mechanical effects we consider here.[37]

Our results for the cohesive energy, lattice constant, bulk modulus, magnetic moment, and pressure derivative of the magnetic moment for ferromagnetic Fe (bcc) and Ni (fcc) are compared to our nonmagnetic results and to experiment in Tables II and III, respectively. Other results of the calculation, such as the spin-polarized density of states, are similar to those found by Callaway and co-workers,[33,34] and will not be discussed here.

The experimental moments given in Tables II and III contain a small orbital part (the g factor is not quite 2), while the calculated results include only the spin moments. If the orbital moment is removed from the experimental values, using the measured g factors,[6] the calculated spin moments are then only 1% too large for Fe, and 5% too large for Ni. The calculated moments are similar to those found by Callaway and co-workers,[33-34] who used the spin-polarized $X\alpha$ method with $\alpha = \frac{2}{3}$. This is an interesting correspondence, given the differences in the approximations used for exchange and correlation.[39] The relatively poor agreement of the calculated pressure derivative of the moment with experiment might be due to the pressure dependence of the orbital part of the

TABLE III. Calculated cohesive energy, lattice constant, bulk modulus, magnetic moment, and pressure derivative of magnetic moment of nonmagnetic and ferromagnetic fcc Ni compared to experiment.

	E_{coh} (Ry)	a (a.u.)	B (Mbar)	$M(\mu_B)$	$\partial \ln M/\partial P$ (kbar^{-1})
Nonmagnetic	0.411	6.55	2.20	...	...
Ferromagnetic	0.419	6.56	2.27	0.59	-2.1×10^{-4}
Experiment	0.326 [a]	6.65 [b]	1.87 [c]	0.61 [d]	-3.0×10^{-4} [e]

[a] Reference 4.
[b] Reference 9.
[c] Reference 14.
[d] Reference 6.
[e] Reference 38.

moment (which is not included in the calculations).

As mentioned earlier, the changes in the calculated nuclear separations correspond to magnetic pressures of 185 for Fe and 8 kbar for Ni. In addition to the decrease in the nonmagnetic part of the bulk modulus caused by the resulting lattice expansion, there are small positive contributions[40] ($\delta B = 60 \pm 30$ kbar for Fe, and 60 ± 50 kbar for Ni) caused by changes in the equation of state due to the magnetism (i.e., the magnetic pressure is intrinsically volume dependent). This small increase is consistent with the effect of spin polarization on the bulk modulus of the homogeneous electron gas.[41]

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[20]This is the result obtained from Heine's expression for the *d* bandwidth, $W \propto 1/a^5$, if we assume $N \propto 1/W$. See V. Heine, Phys. Rev. 153, 673 (1967). According to our band calculations, the exponent is closer to 4 than 5, and values of λ are ~1 for Cr, and ~2 for Mn, Fe, Co, and Ni.

[21]The density-of-states values given in Table I are appropriate to this atomic volume.

[22]The results of our self-consistent calculation thus definitely put Ni to the left of the maximum of the Bethe-Slater curve (exchange parameter vs distance) at 0 K. It is given its traditional position to the right of the maximum on the basis of measurements near T_c (see, e.g., Ref. 14). This may mean that the effective exchange interaction of the localized model is temperature dependent, if only through the thermal expansion.

[23]We used the P_M values of Table I in the nonmagnetic equation of state following from our self-consistent calculations in order to obtain the new lattice constant and bulk modulus. This equation of state was constructed in Bridgman's form $\Delta V/V_0 = -aP + bP^2$ by fitting to self-consistent energy-band calculations at three lattice constants. The resulting values of a and b were of the same order of magnitude as those obtained experimentally by Bridgman (see Ref. 4). Use of Bridgman's values would have given results very similar to those in Table I.

[24]Our nonmagnetic equation of state for (fcc) Mn is clearly inexact, because the bulk modulus remains somewhat too large even if the lattice is expanded beyond its experimental atomic volume. While this might be due to extrapolating over too large a pressure range, the results for Cr and Mn might instead indicate relatively large magnetic changes in the equation of state of antiferromagnets.

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