Stoner theory of magnetic structure of alternate cubic phases of transition metals

J. L. Fry and Y. Z. Zhao
The University of Texas at Arlington, Arlington, Texas 76019

P. C. Pattnaik and V. L. Moruzzi
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

D. A. Papaconstantopoulos
Naval Research Laboratory, Washington, DC 20375

Epitaxial growth of bcc Co on a (110) GaAs substrate has demonstrated the feasibility of producing thin films of transition metals with structures not usually stable at room temperature and pressure. Thus an entirely new group of magnetic materials may be possible with interesting and perhaps significant magnetic properties. In this paper the simple Stoner theory of ferromagnetism is employed, with exchange-correlation parameters obtained from Janak's work and density of states at the Fermi level determined from self-consistent, paramagnetic energy-band calculations. The theory is applied to each of the 3*d* and 4*d* transition metals in both fcc and bcc phases. Ferromagnetism is obtained for bcc Fe, Co, and Mn and fcc Co and Ni, and strongly enhanced paramagnetism for bcc Sc, Ni, and Y and fcc Sc, Fe, and Pd. Comparisons are made with predictions of total energy and enhanced magnetic susceptibility calculations.

I. INTRODUCTION

Magnetism is conspicuous by its absence throughout most of the Periodic Table of elements at standard conditions of pressure and temperature. In the transition metals ferromagnetism is found in hcp Co, bcc Fe, and fcc Ni, and antiferromagnetism in bcc Cr, but no magnetism has been reported for 4*d* or 5d elements. Considerable excitement was thus produced with the report[1] by Prinz of the stabilization of ferromagnetic bcc Co via epitaxial growth on a GaAs substrate. Perhaps there are more magnetic elements in alternate phases which could be stabilized by the same technique, thus opening up the possibility of new and important magnetic materials. In this short paper the possibility of other magnetic 3*d* and 4*d* elements is investigated theoretically.

II. THEORY

The simplest theory which attempts to account for ferromagnetism is the well known Stoner model[2] based upon an enhanced susceptibility

$$\chi = \chi_0/(1 - I\chi_0)\,, \tag{1}$$

where χ_0 is the unenhanced susceptibility and I is an exchange-correlation enhancement parameter. The condition usually taken for ferromagnetism is a pole of this enhanced susceptibility, which can occur whenever the condition $\chi_0 \geqslant 1/I$ is obtained in some elemental metal. Within the random-phase approximation χ_0 is the density of states at the Fermi energy, $D(E_F)$, and the paramagnetic state is unstable if

$$D(E_F) \geqslant 1/I\,. \tag{2}$$

Penn[3] considered a q-dependent enhanced susceptibility and a simple s-band model for transition-metal band structures and studied stability regions in the Periodic Table for ferro- and antiferromagnetism. Asano and Yamashita employed the Stoner theory with a fixed parameter I for the 3*d* elements, used self-consistent energy-band results for $D(E_F)$, and considered both bcc and fcc phases. They used a gap equation to study possible antiferromagnetic phases. The most satisfying theoretical work to understand ferromagnetism in the transition metals was reported by Janak.[5] He employed self-consistent paramagnetic band structures[6] at calculated equilibrium lattice constants and a variational form of the enhanced susceptibility[7] which eliminated all adjustable parameters. His study of 32 cubic elements including 3*d* and 4*d* transition metals correctly predicted the occurrence of ferromagnetism in the normal cubic phases.

III. FERROMAGNETISM

Janak's procedure and some of his results are used here to make a quick determination of possible ferromagnetism in the alternate cubic phases of 3*d* and 4*d* transition metals. $D(E_F)$ was calculated for each 3*d* and 4*d* transition metal in a paramagnetic state using an equal-volume lattice constant for the alternate cubic phase. The calculations were done using an augmented-spherical-wave code[8] with Janak's version of the local exchange-correlation potential.[5,6] $D(E_F)$ was also compared with other existing calculations[9,10] where possible, and with rigid-band estimations. Ferromagnetism is expected to occur where $D(E_F)$ is largest, which is in elements whose Fermi energy falls near one of the peaks which naturally occur for fcc or bcc *d*-electron metals. Near a strong peak care must be taken in calculating both E_F and $D(E_F)$.

In order to use Eq. (1) or (2) it is necessary to compute I. For the first effort this was not done, but the observation made by Janak that I is an atomiclike property, insensitive to crystal structure, was used. This insitivity to crystal structure can be observed by comparing his calculated values of I

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TABLE I. Stoner criteria for alternate cubic phases of 3*d* and 4*d* transition metals. The alternate structures were chosen to be fcc or bcc, whichever does not occur naturally. Lattice constants were chosen to maintain a cell volume equal to the naturally occurring cell volume. For hexagonal metals the alternate cubic phase was chosen to be the one not computed in Ref. 5 of the text. The columns labeled $ID(A)$ and $ID(N)$ are the products I times $D(E_F)$ for the alternate and normal phases, respectively. Ferromagnetism is possible when the product equals or exceeds unity.

	Element	Structure	a (a.u.)	$D(E_F)$ (Ry^{-1})	I (Ry)	$ID(A)$	$ID(N)$
3*d*	Sc	bcc	6.740	31.6	0.025	0.79	0.83
	Ti	bcc	6.004	26.9	0.025	0.67	0.55
	V	fcc	6.980	22.8	0.026	0.59	0.57
	Cr	fcc	6.678	23.2	0.028	0.65	0.25
	Mn	bcc	5.193	33.1	0.030	0.99	0.63
	Fe	fcc	6.489	22.6	0.034	0.77	1.43
	Co	bcc	5.118	50.3	0.036	1.81	0.97
	Ni	bcc	5.198	19.8	0.037	0.73	2.04
4*d*	Y	bcc	7.326	30.8	0.024	0.74	0.46
	Zr	bcc	6.600	16.1	0.023	0.37	0.39
	Nb	fcc	7.812	21.6	0.022	0.48	0.42
	Mo	fcc	7.420	14.9	0.022	0.33	0.20
	Tc	bcc	5.778	21.0	0.022	0.46	0.37
	Ru	bcc	5.715	27.3	0.022	0.60	0.33
	Rh	bcc	5.746	26.6	0.024	0.64	0.43
	Pd	bcc	5.889	19.4	0.025	0.49	0.78

for bcc and fcc Sc, which were identical,[5] $I = 0.025$ Ry. It is thus assumed in this work that I is the same in the alternate phase of each element, and Janak's values are taken.[5]

Table I contains the results of this study. The column labeled $ID(A)$ provides the test for possible ferromagnetic alternate cubic phases using the criterion of Eq. (2). When $ID(E_F)$ exceeds unity the paramagnetic state is unstable with respect to the ferromagnetic phase (it may also be unstable with respect to antiferromagnetic or more complicated order as well). For the alternate cubic phases bcc Co is predicted to be ferromagnetic and bcc Mn almost ferromagnetic. Since the variational theory used to obtain I only ensures that χ in Eq. (1) is the minimum for the assumed form of enhancement,[5,7] it is possible that the tendency for ferromagnetism is underestimated, especially for $ID(E_F)$ near unity. More accurate band calculations, $D(E_F)$ calculations, or determinations of I could result in significantly different predictions for χ. These have been done for fcc Co and predict ferromagnetism.[8] The form of the local exchange-correlation potential used in the self-consistent band-structure calculations may also be a determining factor for these special cases. More complete studies have also been done for bcc and fcc Mn.

For bcc Mn, linear-combination-of-atomic orbitals calculations[10] (LCAO) and augmented-plane-wave[9] (APW) calculations obtained $ID(E_F)$ products which easily exceed unity at the lattice constant used in Table I. A completely different approach[11] to calculating the enhanced susceptibility including the wave-vector dependence has been employed for several transition metals[12] with the conclusion that bcc Mn should be ferromagnetic at this lattice constant. Spin-polarized band calculations using the LCAO method find a stable ferromagnetic moment for bcc Mn,[10] and total-energy calculations as a function of moment and volume confirm this as a stable phase relative to the bcc paramagnetic phase.[13]

Examining Table I for both cubic phases it is seen that only bcc Mn, Fe, and Co and fcc Co and Ni are likely to be ferromagnetic and no 4*d* elements should be ferromagnetic. The latter fact is a consequence of the generally reduced values of $D(E_F)$ and smaller, almost constant values of the integral I in the 4*d* elements. For Fe, Co, and Ni other theoretical predictions have been made through elaborate moment-versus-volume total-energy calculations.[8] At zero temperature, pressure, and applied field these agree with the predictions of Table I and experimental findings. Similar unpublished studies for Mn predict weak ferromagnetism for bcc Mn.[13] Ferromagnetism for bcc Mn has not yet been verified.

Some of the elements exhibit strongly enhanced paramagnetism ($\chi/\chi_0 > 4$) and are likely to display magnetic order at larger lattice constants or upon alloying. These include bcc Sc, Ni, and Y and fcc Sc and Pd.

IV. ANTIFERROMAGNETISM

A simple generalization of Eq. (1) to include a q dependence for χ is possible but this also requires determination of $I(q)$, which is a difficult task. A self-consistent theory for $\chi(q)$ exists and has been applied to some transition metals.[10–12] The many-body enhanced susceptibility is defined by

$$\chi(\mathbf{q}) = \chi_0(\mathbf{q})/[1 - \Lambda\chi_0(\mathbf{q})]\,, \tag{3}$$

where Λ, χ_0, and χ are matrices on a reciprocal-lattice basis. The matrix χ_0 is the random-phase approximation (RPA) susceptibility tensor, Λ is a tensor determined by the local exchange-correlation functional, and χ is the enhanced susceptibility. No adjustable parameters appear in these quantities.[10–12]

If the paramagnetic susceptibility of Eq. (3) has a pole at some q, $\chi(q) \to \infty$, then even in the absence of an applied

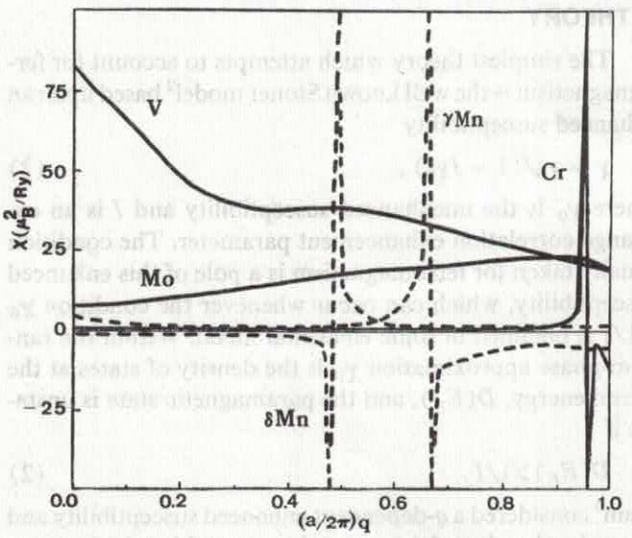

FIG. 1. Exchange-correlation enhanced susceptibility for V, Cr, Mn, and Mo along a cubic axis. For Cr and Mn, χ has been divided by 100 to plot on this scale. δMn is bcc and γMn is fcc.

external field, $H(q)$, $B(q) = \chi(q)H(q)$ may be nonzero, i.e., spontaneous magnetic order may occur. Whether ferromagnetism, antiferromagnetism, or paramagnetism is the stable ground state must be determined experimentally or by total-energy considerations. A simple model[14] relates the change in energy upon magnetic order to the RPA susceptibility χ_0:

$$\Delta E = -K\chi_0(q) \tag{4}$$

with $K > 0$.

Combining Eqs. (3) and (4), a definite prediction of type of magnetic order may be made. For bcc V, Cr, Mn, and Mo and fcc Mn the many-body enhanced susceptibility shown in Fig. 1 predicts that ferromagnetism is possible for bcc Mn, and antiferromagnetism for bcc Cr and fcc Mn. Notably absent is antiferromagnetism in Mo, whose nesting Fermi surface features are identical to Cr. These calculations are very lengthy and are not yet complete for all $3d$ and $4d$ transition metals and will be reported elsewhere.

V. CONCLUSIONS

The Stoner model may be used to predict with relative ease alternate structures which are possibly ferromagnetic and thus stimulate searches for new materials. Alternate ferromagnetic phases predicted in Table I are bcc Mn and Co and fcc Co. Prinz has made ferromagnetic bcc Co.[1]

The generalized Stoner model or $\chi(q)$ is much more expensive to compute, but so far predicts antiferromagnetism for bcc Cr and fcc Mn. The best chance for magnetic order in $4d$ elements should be Mo, but Fig. 1 suggests that it will not occur.

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