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Ferromagnetism in the Transition Metals*

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An outline is given of a proposed theory for the behavior of electrons in transition metals. This is based on considering corrections to a supposed self-consistent band calculation which arise from the intra-atomic electron-electron Coulomb repulsion. The resulting interaction energy is considered to occur only between electrons with similar Bloch wave functions and to depend on the shape of those functions. An important element in the discussion is the one-electron *s-d* admixture term in the Hamiltonian which arises when the *d* band and conduction band are worked out using different potentials. The behavior of dilute alloys of nontransition metals in transition metals can then be understood in terms of the hybridized *s-d* band. It is suggested that the effect of the nontransition impurity (Cu, Zn, etc., are here to be regarded as transition metals) is to lower the conduction band, thus changing the *s-d* band. In terms of a theory parallel to the localized-moment calculation of Anderson, this reduces the magnetic moment by moving the spin-up and spin-down *d* bands with respect to each other. Because of the increased *s*-like character, the true *s-d* electrons have become more mobile and this reduces the effectiveness of the exchange splitting. It is shown that this model leads to reasonable agreement with the experimental reduction in the saturation magnetization. It is further shown that if the interaction energy is regarded as a dominant factor in determining which is the stable lattice structure in these metals, one can obtain correct ranges of stability as the electron-per-atom ratio changes for all three transition series. The second and third series are supposed to be nonferromagnetic because of a large band width and small interaction energy. The paper is entirely qualitative, such calculations as are presented being of an illustrative nature.

I. INTRODUCTION

ONE of the most striking experimental problems still defying satisfactory theoretical description is the phenomenon of ferromagnetism in the transition metals. Many models have been proposed which describe reasonably well certain aspects of the problem, yet for each model there always seems to remain a number of experimental details which cannot be properly treated.[1,2] A fundamental criticism of all these models is that they do not adequately describe the microscopic origin of ferromagnetism, which is still not properly understood. The purpose of this paper is to outline yet another model, which, it is hoped, might be capable of leading a little closer to a true understanding of the behavior of electrons in the transition metals. At the very least, it suggests a difference in emphasis which might help improve some of the earlier models.

This paper is directed primarily at discussing the alloys of transition metals with nontransition elements, in particular their magnetic properties. In order to do this it is necessary first to outline a model of transition metal ferromagnetism within which such a discussion can be held. In fact this will occupy the bulk of the paper. The arguments are entirely qualitative; it is improbable that a quantitative version could be completed within the present day understanding of correlation effects in a medium-density electron gas.

The principal physical features involved in the following pages are:

(1) The interaction favorable to magnetic alignment of electrons derives from intra-atomic *d*-electron–*d*-electron Coulomb repulsions which are larger between electrons of unlike spin than between electrons of like spin. The unusual feature here is that it will be argued that any given electron interacts in this way with only a very limited number of other electrons (those having energies sufficiently close to that of the electron in question). These are distributed irregularly through the crystal.

(2) The principal deterrent to ferromagnetism is then the normal increase in one-electron energy as the occupation numbers for different spins become unequal. A second effect, which can be viewed in two equivalent ways, is due to admixture with the conduction electrons. The correct wave function, involving both *s* and *d* components, is more evenly spread through the lattice than a pure *d* function so that the interaction energy discussed in (1) above is smaller. Increasing the *s* component reduces the interaction, and hence the magnetic moment if any, still further. Alternatively one may regard the electrons as undergoing transitions between *s*- and *d*-like character. The interaction is then fixed for the *d*-like electrons, but as the transition rate increases the electrons feel the interaction for smaller portions of their time. This latter approach is the more amenable to calculation.

(3) Alloys between transition metals and nontransition elements can then be understood in terms of the model[3] in which the *d* electrons are confined to the transition metal sites in the crystal, the *d* band in consequence being narrowed without change of shape.[3,4]

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[1] A comprehensive review together with an extensive bibliography has been given by N. F. Mott, Advan. Phys. **13**, 325 (1964).

[2] H. Brooks, in *Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by Paul A. Beck (Interscience Publishers, Inc., New York, 1963).

[3] J. L. Beeby, Phys. Rev. **135**, A130 (1964).

[4] E. A. Stern (to be published).

TABLE I. The experimental and theoretical results for the solute concentration at which the low-concentration saturation magnetization extrapolates to zero. The number of sub-bands supposed participating in the magnetization is also given.

Alloy	Experimental results	No. of bands	Theoretical results
Fe-Al	100	3	55.5
Fe-Si	100	3	47
Co-Al	33	3	35
Co-Si	31	3	27.5
Ni-Al	21.5	2	13
Ni-Si	16	2	9.5

The valence electrons introduced by the impurity contribute to the conduction band which in turn screens the impurity potential. The increase in the number of conduction electrons will then increase the *s-d* admixture and, as discussed in (2) above, this will lead to a reduction in the magnetic moment by moving the spin-up and spin-down *d* bands closer together in energy. Though it is, in principle, important how the screening takes place, the admixture being different if some of the conduction electrons are localized, the work to follow is too crude to reflect this point. Note that in this sense Cu, Zn (and Ag, Cd, Au, and Hg) are *transition* metals when in dilute solution, their *d* band being involved in the alloying process.

(4) The question which of the lattice structures (bcc, fcc, or hcp) should be stable in any given case is not easily discussed for the transition metals. If, however, one considers the interaction energy to be the primary difference between the structures, the Slater-Pauling curve and the ranges of stability in the three transition series are found to be related in a natural way. The important feature here is the suggestion, which arises in the analysis of point (1) to follow in the next section, that the interaction energy varies rapidly with wave function localization. This latter quantity varies with the energy of the electron concerned, the range of variation probably being much less in the fcc system than in the bcc system.

A question which should be answered at once regarding this model, in which the transition metal magnetic moment is reduced by increased *s-d* admixture, concerns the magnitude of the effect. The following interesting results arise from the crude calculation of this point to be presented in Sec. IV:

(i) Though, at first sight, the effect seems likely to be a small one, surprisingly good agreement is obtained with the experimental results on the alloys of Fe, Co, and Ni with Al and Si as may be seen in Table I.

(ii) Essentially no free theoretical parameters need be assumed to obtain this result; it does not depend on the magnitude of the interaction energy nor on any parameters of the admixture. This is true only for the change in the magnetization, any prediction of the magnetic moment itself would require a knowledge of these values.

(iii) The predicted valence dependence of the result, the change in magnetization being proportional to $(v-n_s)$, where v is the impurity valence and n_s the number of conduction electrons per transition metal atom, agrees very well with experiment, especially for the Ni alloys. This should be contrasted with proportionality to v arising from the usual model[1] in which the *d* band is filled by the valence electrons of the impurity.

Points (1) to (4) will be discussed sequentially in the following sections.

II. THE INTERACTION ENERGY

The concern of this section is an attempt to understand which parts of the electron-electron Coulomb energies have been included incorrectly or inadequately in a supposedly self-consistent band calculation. If the self-consistency is at all reasonable, the potential involved will be, in each unit cell, not very different from an ionic potential. Thus, the usual types of transition metal band calculation are appropriate. The *d* electrons on a given ion are, however, actually subject to strong correlations so that an electron moving in the neighborhood of the ion will be influenced by the specific distribution of electrons there. There are many possible distributions, just as there are many configurations possible in a free ion. These distributions will not, in general, be arranged in an orderly fashion (this would be observable, e.g., in neutron scattering) but will be distributed in some way throughout the crystals. Despite the lack of periodicity, a band calculation in such a system is still possible provided that the energies of the electron in the presence of the various distributions are sufficiently close together. The wave function in this case should be thought of as adjusting itself to each particular distribution passed by the electron on its way around the crystal.[3]

It is useful at this point to observe that with a few exceptions the neutral atom energy levels depend only weakly on the outer electron configuration, so that a band-type calculation using atomic potentials is not unreasonable.[1,5] From this point of view it is not important that the individual electron-electron correlation energies are large since the over-all electrical neutrality suggests that the total energy at a given site does not depend strongly on the number of *d* electrons there. In this way the self-consistent theory can adequately represent the bulk of the correlation energies. On the other hand, those atomic configurations having energies significantly different from the "average" energy used in the self-consistent calculation will require modification of the band calculation. The simplest way to do this is to add an "interaction term" to the Hamiltonian, but because the necessary mathematical techniques do not exist this must be done in a somewhat arbitrary manner. One can interpret the atomic situation by

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[5] C. Herring, J. Appl. Phys. Suppl. **31**, 3S (1960).

supposing that a pair of electrons are able to stay sufficiently far from each other to avoid the majority of the Coulomb energy except when their wave functions are related in some special way. The naive view will be taken here that this special relationship occurs when the wave functions would have been, in the absence of the Coulomb potential, very much alike.

This atomic viewpoint, used by way of illustration, requires some modification for the transition metals where the electron wave functions are Bloch-like functions which can be considerably different from atomic functions even inside the unit cell. A further consideration arises from an important consequence of the disorderly arrangement of the various distributions. This is the introduction of an imaginary part into the energy[6] which modifies the band calculation discussed above essentially by transforming the Bloch functions into wave packets with dimension depending on the disorder. The success of the itinerant electron theory indicates that the wave packets cover many unit cells, so that the wave function within any given unit cell is similar to that of a Bloch function. Nevertheless the conceptual picture is altered and is best regarded as time-dependent. The wave packets move about undergoing various transition processes; the resultant electronic distribution in any one cell depends on those wave packets near the cell and necessarily changes with time. If the wave packets, supposed derived only from *d*-type Bloch functions, are denoted by the quantum index p, the energy may be written:

$$H_{\text{band}}=\sum_{p,\sigma} E_p n_{p,\sigma}. \tag{1}$$

Here $n_{p,\sigma}=\eta_{p,\sigma}{}^\dagger\eta_{p,\sigma}$ is the occupation number for the wave packet p with energy E_p and spin σ. The index p refers to the position, energy, and effectively to the band number of the wave packet. The set p will vary with time.

Now suppose one follows the assumption above, that the Coulomb effects between two electrons lead to interactions only when their wave functions are very similar. Consider only the *d* functions. Within a given unit cell the wave function of the wave packet is like a Bloch function, so wave packets can only interact in this way when their energies are very close together. For only in this case (neglecting complications due to multiple bands) are the Bloch functions similar. Also, the Pauli principle will ensure that electrons of the same spin will not approach so closely as electrons of opposite spin, so the interaction is predominantly between electrons of opposite spin. The interaction thus has the form

$$H_{\text{int}}=\sum_{p,p'} U(p,p')n_{p,\uparrow}n_{p',\downarrow}. \tag{2}$$

The potential function $U(p,p')$ will increase as the electrons p and p' overlap more, its range will be of the order of the wave packet size. One may deduce two further properties of U from the way the interaction energy was described as arising. U will decrease rapidly as p and p' become different in energy, the wave functions no longer being sufficiently alike and $U(p,p')$ will increase rapidly as the wave function corresponding to p becomes more localized at the cell center. One may estimate from the variation in energy of the atomic configurations that the magnitude of the interaction energy will be 1–4 eV/atom.

This then is the model to be used. Any attempt to improve upon this discussion is beset by many difficulties, several of which have been discussed by Hubbard.[7] The self-consistent calculation, for example, requires a more accurate description of the wave functions in the disordered system than is at present possible.

III. ADMIXTURE WITH THE CONDUCTION BAND

It is important that the conduction electrons were not included in the discussion of the previous section since no estimate could have been made of the change in U due to the alteration in the wave function caused by hybridization. So the conduction band must be worked out separately and will give rise to the Hamiltonian

$$H_0=\sum_l \epsilon_l c_l{}^\dagger c_l, \tag{3}$$

where $c_l{}^\dagger$ will denote the creation operator for the state l with energy ϵ_l. If the Hamiltonian in the absence of any interaction is H, then the eigenstates of H divide approximately into two groups; *d*-like and conduction-like states. The band calculation leading to the *d*-band Hamiltonian (1) should give a reasonable approximation to the first group, the conduction states as defined in Eq. (3) to the second group. It will now be indicated how admixture between these states can lead to a further one-electron term in the Hamiltonian. It is not appropriate to carry out a rigorous derivation here since H, H_{band}, and H_0 would need to be more accurately defined, and in any case only a crude averaged value for the admixture is used in the calculation. Consider the first group of true states and denote them by creation operators $t_d{}^\dagger$. The difference between $t_d{}^\dagger$ and the *d*-state $\eta_p{}^\dagger$ of appropriate energy is a conduction-like admixture in the true state:

$$t_d{}^\dagger=\eta_p{}^\dagger+\sum_l v_{lp}{}^* c_l{}^\dagger$$

apart from normalization factors. The v_{lp} should be small except for the limited number of states with strong conduction and *d*-like admixtures, and may be calculated, e.g., by perturbation theory. Thus, that part of the true Hamiltonian due to this group of states is

$$\begin{aligned} H^{(1)}&=\sum_d E_d t_d{}^\dagger t_d \\ &=\sum_p E_p(\eta_p{}^\dagger+\sum_l v_{lp}{}^* c_l{}^\dagger)(\eta_p+\sum_l v_{lp}c_l), \end{aligned}$$

which, to first order in v, is H_{band} plus the admixture term $\sum_{p,l} E_p v_{lp}{}^* c_l{}^\dagger \eta_p+\text{c.c.}$ The second group of states

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[6] S. F. Edwards, Proc. Roy. Soc. (London) **A267**, 518 (1962).

[7] J. Hubbard, Proc. Roy. Soc. (London) **A277**, 237 (1964).

leads to $H^{(2)}$ in the form H_0 plus a similar admixture term. Thus the hybridization can be approximated by a term in the Hamiltonian of the form

$$H_{s\text{-}d}=\sum_{l,p}(V_{lp}c_l^\dagger\eta_p+V_{lp}^*\eta_p^\dagger c_l). \tag{4}$$

The total Hamiltonian is thus $H_T=H_0+H_{\text{band}}+H_{\text{int}}+H_{s\text{-}d}$ and is very similar in form to the Hamiltonian used by Anderson[8] for a localized d state in a sea of conduction electrons. The formalism is identical in outline to Anderson's and depends on the approximate equation for the d state:

$$[H,\eta_{p,\sigma}^\dagger]=[E_p+\sum_{p'}\langle U(p,p')n_{p',-\sigma}\rangle]\eta_{p,\sigma}^\dagger+\sum_l V_{pl}c_{l\sigma}^\dagger, \tag{5}$$

where the Dirac brackets here denote an ensemble average. The calculation now proceeds by writing down equations for the matrix elements of the Green function

$$G(E+i\epsilon)=(E+i\epsilon-H)^{-1}, \tag{6}$$

in terms of which the total density of states is given by

$$\rho^\sigma(E)=-(1/\pi)\,\mathrm{Im}[\mathrm{Tr}G^\sigma(E)]. \tag{7}$$

It is then straightforward to calculate the matrix elements involving the d states[8]:

$$G_{p',p}{}^\sigma=[(E-\epsilon_{p',\sigma})\delta_{p'p}-\sum_l V_{p'l}(E-\epsilon_{l,\sigma})^{-1}V_{l,p}]^{-1}, \tag{8}$$

where

$$\epsilon_{p,\sigma}=E_p+\sum_{p'}\langle U(p,p')n_{p',-\sigma}\rangle. \tag{9}$$

The last term in the denominator of Eq. (8) represents the effect of admixing conduction states into the d states. Since the major interest will be in the occupation numbers $n_{p,\sigma}$ the off-diagonal terms, mixing states p and p', are not very important. The real part of the admixture term may also be neglected since it may be assumed absorbed into E_p. Thus, the diagonal elements are given by

$$G_{p,p}{}^\sigma=[E-\epsilon_{p,\sigma}+i\Delta_p]^{-1}, \tag{10}$$

where

$$i\Delta_p=i\pi\sum_l|V_{lp}|^2\delta(E-\epsilon_l)\cong i\pi\langle|V_{lp}|^2\rangle\rho_s(E) \tag{11}$$

and $\rho_s(E)$ is the density of conduction states of energy E. The approximate equality in Eq. (11) arises from the supposition that $|V_{l,p}|^2$ is sensitive only to the energy of the states l, the average then being over all states on the surface of energy E. Equation (10) shows that the d level has broadened to Lorentzian shape with width Δ_p. The total d-state density is thus

$$\rho_d{}^\sigma(E)=\frac{1}{\pi}\int\frac{\Delta_p}{(E-\epsilon_{p,\sigma})^2+\Delta_p{}^2}\rho_d{}^0(E_p)dE_p,$$

showing that the pure d-band density of states $\rho_d{}^0(E_p)$ has been smoothed by the width function Δ_p. Δ is probably of order 1 eV. The probability of occupation for the state p, σ is given by

$$n_{p,\sigma}=\frac{1}{\pi}\int_{-\infty}^{\epsilon_F}\frac{\Delta_p}{(E-\epsilon_{p,\sigma})^2+\Delta_p{}^2}dE=\frac{1}{\pi}\cot^{-1}\frac{\epsilon_{p,\sigma}-\epsilon_F}{\Delta_p}.$$

One has then for $\epsilon_{p,\sigma}$ given by Eq. (9)

$$\epsilon_{p,\sigma}=E_p+\int\rho_d{}^0(E_{p'})U(p,p')\frac{1}{\pi}\cot^{-1}\frac{\epsilon_{p',-\sigma}-\epsilon_F}{\Delta_{p'}}dE_{p'} \tag{12}$$

and this gives a pair of self-consistent equations to be solved for $\epsilon_{p,\sigma}$. Ferromagnetism then depends on whether $n_+=\int\rho_d{}^0(E_p)n_{p,+}dE_p$ is the same as n_- or not. As an example one may reduce to the special case given by Anderson[8] by choosing $U(p,p')=U=\text{constant}$, $\rho_d{}^0(E_{p'})=\delta(E_{p'}-E_0)$, $\Delta_{p'}=\Delta=\text{constant}$. The presence or absence of ferromagnetism then depends on the parameter U/Δ, larger U/Δ being more favorable to ferromagnetism. Some curves are drawn in Fig. 1. If one really understood the functional forms of the parameters required in Eq. (12) it would be possible to evaluate the saturation magnetization predicted by this model. This is not possible, but in the next section a qualitative discussion of the effects of alloying will be presented and it will be seen that *changes* of magnetization are not too sensitive to the parameters involved.

IV. ALLOYS WITH NONTRANSITION METALS

Dilute alloys of nontransition metals with transition metals can show a wide variety of behavior depending on which transition metal is the host. The remarks of this section are mainly directed towards magnetic properties and are thus principally concerned with the first transition series. Consider the saturation magnetization of Fe, Co, and Ni upon alloying with Al or Si. The Fe alloys show a saturation magnetization decreasing as though simple dilution is taking place, i.e , the magnetic moment per Fe atom stays constant.[9,10] In Ni alloys the magnetization decreases rapidly, roughly as though the d-band were being filled by the solute conduction electrons.[11,12] Finally in Co alloys the decrease in magnetization is so fast that there are too few solute conduction electrons to fill the d band quickly enough.[9,12] The results of the last section, severely truncated in order that some numbers can be obtained, will now be shown to give a reasonable qualitative understanding of these experimental facts.

Since the d band is supposed to change only by becoming narrow on dilution with nontransition elements and the Fermi level must remain approximately constant in a dilute alloy, the important change is in the

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[8] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[9] D. Parsons, W. Sucksmith, and J. E. Thompson, Phil. Mag. 3, 1174 (1958).

[10] C. H. Cheng, K. P. Gupta, C. T. Wei, and P. A. Beck, J. Phys. Chem. Solids **25**, 759 (1964).

[11] J. Crangle and M. J. C. Martin, Phil. Mag. 4, 1006 (1959).

[12] J. Crangle, in *Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by Paul A. Beck (Interscience Publishers, Inc., New York, 1963).

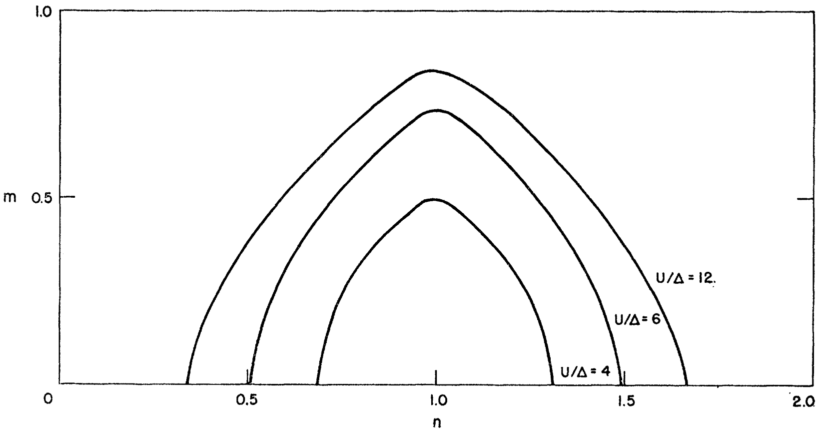

FIG. 1. The value of the saturation magnetization m as a function of the number of electrons n in Anderson's model. Three values of U/Δ are illustrated.

conduction band. The conduction electrons, in fact, move in a potential which is the same at each host site as in the pure metal but is much larger at each solute site. To completely screen the solute potential needs a number of electrons equal to the valency of the solute, and these must lie in the conduction band and be below the Fermi level. This is just like an alloy between two nontransition metals, but the attendant complications may be avoided because only an average of the matrix elements V_{lp} is required and this should be rather insensitive to details of the wave functions. It is thus qualitatively satisfactory to use a free-electron-like conduction band as will now be done.

One needs to calculate the lowering dE of the bottom of the conduction band E_0 to accommodate the extra electrons introduced by the impurities. If there are n_s conduction electrons per host atom and v per solute atom, the conduction band contains

$$n_{dc}=n_s(1-dc)+vdc=n_s+(v-n_s)dc$$

electrons per site in an alloy with concentration dc of impurities. If the Fermi energy is ϵ_F and the effective mass α then

$$n=\int_{E_0}^{\epsilon_F}\alpha(E-E_0)^{1/2}dE=2\alpha(\epsilon_F-E_0)^{3/2}/3$$

is the band occupation. The width function Δ, defined by Eq. (11), now varies according to

$$\frac{d\Delta}{\Delta}\simeq\frac{d\rho}{\rho}=\frac{\partial\rho}{\partial E}\left(\frac{dE}{\rho}\right).$$

It is here assumed that $|V|^2$ is not appreciably changed by the impurities. Since there are $(v-n_s)dc$ extra electrons

$$dE=dc(v-n_s)/\rho(\epsilon_F).$$

Combining these results one has

$$\left.\frac{d\Delta}{\Delta}\right|_{\epsilon_F}=\frac{dE}{\rho}\,\frac{\alpha}{2(\epsilon_F-E_0)^{1/2}}=\frac{(v-n_s)dc}{\rho^2}\,\frac{\alpha}{2(\epsilon_F-E_0)^{1/2}}=\left(\frac{v-n_s}{3n_s}\right)dc \quad (13)$$

for the fractional change in the parameter Δ.

The final step is the calculation of the change in magnetization due to this increase in admixture. Detailed results, using Eq. (12) are out of the question, but as an illustration it is interesting to consider a crude model. In this the d band is regarded as split into five bands, each independently satisfying Eq. (12) for the special case solved by Anderson. Then the magnetization of each band in the strong-correlation case ($U\gg\Delta$) is given by[13]

$$m=1-[\pi yx(1-x)-1]^{-1},\quad y=U/\Delta,$$

where x depends on the filling of the band. When m is not zero this gives

$$dm/dy=(1-m)(2-m)/y.$$

The total magnetization will be given by $M=\sum_{i=1}^{5}m_i$ so that

$$\frac{dM}{dy}=\frac{1}{y}\sum_{i=1}^{5}{}'(1-m_i)(2-m_i)=\frac{A}{y} \quad (14)$$

defining A. The prime on the summation indicates that only bands with $m_i\neq 0$ have been included. Thus one has at last

$$\frac{dM}{dc}=\frac{dM}{dy}\,\frac{dy}{d\Delta}\,\frac{d\Delta}{dc}=\frac{A}{y}\cdot\frac{-y}{\Delta}\cdot\frac{\Delta(v-n_s)}{3n_s}=\frac{-A(v-n_s)}{3n_s} \quad (15)$$

for the change in the host bands due to the increased admixture. To this must be added the dilution effect. This result depends only on the solute valence, the

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[13] Equation (30) of Ref. 8.

number of conduction electrons per host atom and, through A, on the sub-bands of the solvent. All other parameters have dropped out. Table I indicates the results of a comparison with experimental values which in view of the many crude approximations involved must be regarded as satisfactory. A was calculated assuming n bands were involved equally in the magnetization so that $A=n(1-M_0/n)(2-M_0/n)$. n, given in Table I, was guessed empirically, mostly by reference to the Slater-Pauling curve. More details on this point will be found in the next section. n_s was taken to be 0.55 and $M_0=2.12, 1.61$, and 0.55 for Fe, Co, and Ni, respectively.

Roberts *et al.*[14] have carried out experimental work on the Mössbauer effect for ^{197}Au alloys and these included some Ni-Au alloys. They correlated the measured isomer shift with the residual resistivity and were forced to the conclusion that the Au ion in Ni is, if anything, negatively charged. This, coupled with the absence of any change in slope in the isomer shift when the Au concentration passed through 60%, strongly suggests that the d band is in no sense being filled as the Au concentration increases. Although Au was carefully excluded from the above analysis because its d band might be important in the alloying behavior, the work of Roberts *et al.* indicates that the d levels of Au do not become part of the Ni d band. If this is so then the theory developed above can be applied to Ni-Au. The theory then predicts 45% for the concentration at which the saturation magnetization goes to zero compared with 60% experimentally. Determining the parameter A empirically for the three Ni alloys, thus checking the $A(v-n_s)/3n_s$ dependence, one obtains for Ni-Au, Ni-Al, and Ni-Si, the values 1.36, 1.35, and 1.38, respectively, for A demonstrating that the valence dependence is correct. For Ni-Cu, on the other hand, $A=1.65$. Thus, Au and Cu when alloyed into Ni reduce the Ni magnetic moment by entirely different processes.

The process suggested should be reflected in the low-temperature specific heat, through the density of states. To emphasize this consider the difference between Ni-Al and Ni-Cu. In the latter alloys the d band is being filled so that the density of states should decrease following the shape of the band. In Ni-Al, on the other hand, the two d bands move with respect to one another and even after the saturation magnetization has gone to zero should still lead to a large specific heat. Because, however, the alloys are only solid solutions for small (of order 10%) solute concentrations, this last remark cannot be verified from available experimental data. Unfortunately, the densities of states in the transition metals themselves are not unambiguously determined by the experimental specific heats because of magnetic effects.[15]

Any improvement over this numerical calculation should be carried out by reference to Eq. (12) rather than by patching up details of the foregoing. The improved calculation would show some differences between the middle and edges of the d band, since the effect of admixture is only to smooth the middle of the band while at the edges some considerable changes take place. The above applied most nearly to the "edge" case; in Fe, for example, considerably less rapid decrease in magnetization would be predicted by Eq. (12) than is suggested in Table I.

V. DIFFERENCES BETWEEN THE LATTICE STRUCTURES

The interaction energy of Eq. (2) is the net gain in energy due to the electron-electron Coulomb potential after the wave functions have deformed to reduce the energy so far as is possible. More accurately, it is the net gain minus some average energy which was used in the self-consistent one-electron calculation. The more the wave functions must deform the larger is this net gain in energy likely to be. Thus it seems reasonable that the interaction energy increases rapidly as the (similar) Bloch wave functions of the two electrons become more localized in space. It will be indicated in this section that from the point of view of localization the bcc and fcc lattices are dissimilar and this leads to a natural relationship between the Slater-Pauling curve and the stable lattice structures. Tight-binding theory will be used, the calculation nearest in spirit to the procedure considered here being that of Asdente and Friedel.[16] The band structure is defined by[17]

$$\det[(E-E_0)J_{\alpha\beta}(\mathbf{k})-h_{\alpha\beta}(\mathbf{k})]=0\,,\quad \alpha,\beta=1,\cdots 5\,.$$

Here E_0 is the bound-state energy in the cell potential and J and h are overlap integrals of order zero and one, respectively, in the potentials. For the bcc case calculations[16,18,19] have shown that the radial behavior depends strongly on energy and rather less on other factors. The general form is then that the lowest two of the five bands thus defined are of bonding type and fairly narrow, the upper two being again narrow but of antibonding type. The middle band is broader and of mixed type.[1]

This does not seem to be true to the same degree in the fcc case, the difference being essentially that of the geometry of the nearest neighbors. Consider $h_{\alpha\beta}{}^0$:

$$h_{\alpha\beta}{}^0=\sum_{\mathbf{R}'\neq 0}\int\phi_\alpha(\mathbf{r})U(\mathbf{r}-\mathbf{R}')\phi_\beta(\mathbf{r})d\mathbf{r}\,,$$

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[14] L. D. Roberts, R. L. Becker, F. E. Obenshain, and J. O. Thomson, Phys. Rev. **137**, A895 (1965), L. D. Roberts and J. O. Thomson, *ibid.* **129**, 664 (1963). I am grateful to Dr. Roberts for bringing my attention to these points.

[15] If solid solutions could be obtained with solute concentration much higher than the concentration at which the magnetization goes to zero, it might be possible to measure the density of states to check this result. Professor Beck has suggested that it might be possible to obtain some Ni alloys satisfying this condition.

[16] M. Asdente and J. Friedel, Phys. Rev. **124**, 384 (1961); **126**, 2262 (E) (1962).

[17] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1956), Sec. 4.2.

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[19] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

where $\phi_\alpha(\mathbf{r})$ are the bound d-wave functions in the potential $U(\mathbf{r})$. This may be regarded as a first-order energy shift, which because of the increased angular cancellation and (for the same density) larger nearest-neighbor distance tends to be smaller in the fcc case. As an illustration consider two lattices, bcc and fcc, of the same density, with the same potential in the unit cell. Evaluate $h_{\alpha\alpha}{}^0$ for $\phi_\alpha(\mathbf{r})=(1/N)(xy/r^2)re^{-\lambda r}$, $\mathbf{r}$ outside the unit cell. For nearest neighbor $\mathbf{R}'$ the dominant contribution will come from the region near $\mathbf{R}'/2$ where for $(xy/r^2)^2$ one has $(d=|\mathbf{R}'/2|)$:

$$\begin{aligned} &\text{(i) bcc} && x^2=y^2=z^2=(d/2)^2/3\,, && && x^2y^2/r^4=\tfrac{1}{9} && \text{(8-fold)}\,,\\ &\text{(ii) fcc} && x^2=y^2=(d/2)^2/2\,, && z^2=0\,, && x^2y^2/r^4=\tfrac{1}{4} && \text{(4-fold)}\,,\\ & && x^2=z^2=(d/2)^2/2\,, && y^2=0\,, && x^2y^2/r^4=0 && \text{(4-fold)}\,,\\ & && y^2=z^2=(d/2)^2/2\,, && x^2=0\,, && x^2y^2/r^4=0 && \text{(4-fold)}\,, \end{aligned}$$

so that for the sum over all nearest neighbors

$$\begin{aligned} &\text{(i) bcc} && \textstyle\sum(x^2y^2/r^4)=8/9\,,\\ &\text{(ii) fcc} && \textstyle\sum(x^2y^2/r^4)=1\,. \end{aligned}$$

In this approximation there are no off-diagonal terms in either lattice and the two terms corresponding to wave functions of (x^2-y^2) type are zero for the bcc system. Thus the greater number of fcc nearest neighbors is almost completely offset by their angular distribution. When λ corresponds to a binding energy of more than 4 eV the bcc shift is already the larger when one allows for the slightly greater nearest-neighbor distance in the fcc case. Asdente and Friedel[18] have drawn attention to the band structure changes caused by these shifts. What is happening is that in the bcc case the xy-type wave function can gain considerable energy by spreading into the neighboring sites; the angular distribution of neighbors is helpful in this respect. The result is a well spread out wave function and large h^0. Conversely, the (x^2-y^2)-type wave functions cannot be matched appropriately at the cell boundaries and thus become more localized than the original atomic functions. In the fcc case the nearest neighbors are more spherically situated, the deviations from atomic-like radial distributions being much less than in the bcc lattice. Because of this the bottom of the bcc band is lowered with respect to the bottom of the fcc band and the top stays above the fcc band top. This effect therefore emphasizes any difference between the bands (which is most likely in the same direction) caused by the rest of $h_{\alpha\beta}$ and suggests that the bcc band is the broader of the two. One must be aware that the original self-consistent calculation is sensitive to the sort of band structure differences just discussed and could amplify them considerably.

For bcc crystals one thus has at the bottom of the band relatively flat Bloch wave functions (in a radial sense) for which $U(p,p)$ is small. As one goes further up the band the interaction energy begins to increase until at the top of the band it is very large because the radial part of the wave function is strongly contracted towards the cell centers. The Slater-Pauling curve for saturation magnetization as a function of the e/a ratio can then be understood as follows. Because U is small for (say) the bottom two-fifths of the band there is no magnetization until there are already four d electrons per atom. After this at some value of band-filling U will become large enough for magnetization to be favorable. At this point $e/a-n_s>4$. The electrons will then fill only one spin band until it is fully occupied at which point $e/a-n_s>7$ (5 electrons of one spin plus at least two of opposite spin). A complementary effect here is that in Sc, Ti, and perhaps even V the d electrons can not really be considered tightly bound, their band width is too large and this helps suppress the magnetism for those elements. After the maximum the extra electrons will go into the empty band leading to a linear decrease in magnetization. In other words, only between two and three fifths of the electrons will participate in the magnetic behavior of the bcc metals, hence the use of $n=3$ for Fe in Table I.

The interaction energies and the energy shifts $h_{\alpha\beta}{}^0$ of the band are so large (eV) that they will play a dominant role in determining the stable lattice structure for any given e/a ratio. The bcc and fcc lattices at a given density are so similar that all differences other than those which may be considered one-electron energies may be supposed small. Thus, one assumes that the self-consistent fields are similar and that the numbers of valence electrons are the same so one need not worry about multiple counting of interactions. The comparison between the lattices is now possible by computing total one-electron energies plus interaction energies. For low-e/a values the bcc system has no interaction energy plus a very low band energy. The fcc system, even if it had polarized bands, i.e., was ferromagnetic, to avoid the interaction energy, has higher band energies. Thus it is basically the low-band energy which stabilizes the bcc system. (This low energy is, of course, enhanced in the self-consistent calculation by the low total interaction energy of the smoother wave functions.) When the d band is nearly full, however, the bcc system is subject to a very large interaction energy. This can be reduced by ferromagnetic splitting of the band, but once the second-half of the band starts to fill the lattice rapidly becomes unstable with respect to the fcc. This is indeed what happens, the bcc range of stability stops just after the peak in the Slater-Pauling curve. The hcp structure can be included in this system by regarding the hcp structure as intermediate between the bcc and fcc structures, having roughly one-fifth of a band with negligible interaction energy and a maximum interaction energy intermediate between the other two.

The nonmagnetic situation implies that the interaction energy can not be avoided because to do so would increase the band energy by an even greater amount. This depends on the ratio of the bandwidth to the interaction energy. Now in the second and third transition series the bandwidth appears to be larger than in the first series, reflecting the larger radius of the ionic

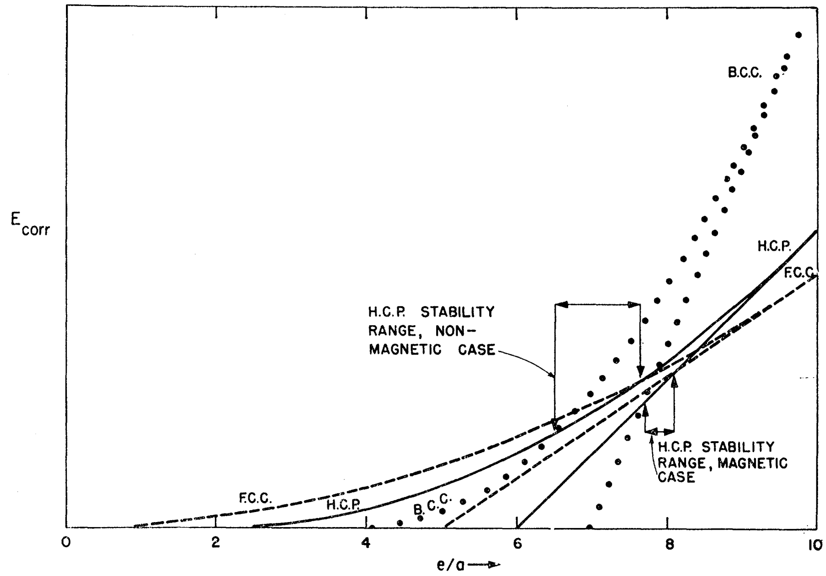

FIG. 2. The total interaction energy E_{corr} as a function of electron/atom ratio in the ferromagnetic and nonferromagnetic cases. The bcc, hcp, and fcc structures are represented respectively by the dotted, solid, and dashed curves.

d-wave functions. This also suggests a much reduced interaction energy because of the greater volume occupied by the electrons. From the outlook of this paper this is the reason that the second and third series are not ferromagnetic. But in the absence of ferromagnetism the larger interaction energy of the bcc system enters the total energy at much lower e/a values so that the lattice becomes unstable with respect to the fcc system at much lower e/a values, as is observed.

Figure 2 illustrates the behavior of the interaction energy alone, denoted by E_{corr}, for the magnetic and nonmagnetic cases. The model used is one in which for the bcc, hcp, and fcc lattices there are respectively 3, 4, and 5 fifths of the band with nonzero interaction energies $U(p,p)=U''$, U', and U. The ratios U''/U' and U'/U are chosen so that the hcp phase is stable for e/a lying between 7.6 and 8.1. It is then seen that both phase changes occur at much lower e/a values in the nonmagnetic case and that the hcp phase then has a larger range of stability, as is observed experimentally. This demonstrates that the general model of interaction energies outlined at the beginning of this paper can be made to give excellent qualitative agreement with experiment by regarding such interaction energies as the dominant features of the lattice structures.

VI. CONCLUSION

It has been shown that a model in which the saturation magnetization of an alloy is dependent on the *s*-*d* admixture can lead to reasonable agreement with experiment. In order to calculate the changes in saturation magnetization it was necessary to put forward a model for the origin of the ferromagnetism. This model, though very crude, nevertheless suggests important differences between the bcc and fcc lattices, principally in the behavior of the electron-electron interaction energy. Regarding the interaction energy as being the dominant effect in determining the stable lattice structure leads to the correct ranges of stability for the lattice structure as e/a varies for both the ferromagnetic and nonferromagnetic series.

It is clear that an improved version of the itinerant electron model calculation is necessary. This should include the hybridization of the bands, both *s* and *d* bands being those for the alloy in question. Some model of the exchange energy must be postulated, such as is proposed in this paper; unfortunately, a better derivation of the exchange energy is a problem of considerable mathematical complexity. Even in the absence of such a first principle calculation of the exchange energy, it is evident that the existing experimental data, especially that concerning the alloys, contains a great deal of information which can be used to resolve some of the remaining difficulties concerning the *d* electrons.

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