ropy. The single-ion anisotropy due to the low symmetry of the crystalline fields at the Fe^{3+} sites is also probably large.

In regard to the linewidth, the large anisotropy is not readily understood. The observed behavior is similar to that expected from a "polycrystalline" sample in which all the crystallographic axes of the individual crystallites are nearly parallel. In this case, the narrowest linewidths would be observed for an external field direction in which the internal fields contributed least to the resonance field, i.e., the a direction for gallium iron oxide. The linewidth maxima in the b and c directions at 270°K are perhaps associated with spin fluctuations due to the nearness in temperature of the broad ferrimagnetic-paramagnetic transition. Here again, one would expect the smallest effect for the a direction.

As to the various mechanisms which contribute to the magnitude of a ferrimagnetic resonance linewidth, many may be ruled out as being too small to explain the large observed linewidths. These include surface pit scattering and scattering due to random atomic disorder. The magnitude of ΔH is, however, not inconsistent with two-magnon scattering if there are long-wavelength fluctuations of the internal fields.[14] This is a result of the fact that fluctuations which correspond to the wavelengths of magnons degenerate with the $k=0$ magnons give rise to a greatly enhanced scattering. Such fields may arise from strains in the vicinity of dislocation lines and impurity atom clusters via magnetostriction. For $Ga_{2-x}Fe_xO_3$ in particular, it is conceivable that the value of x itself varies over distances of the order of several hundred lattice spacings.

ACKNOWLEDGMENTS

I would like to thank V. J. Folen and G. T. Rado for many valuable discussions. The single crystals employed were grown by R. A. Becker.

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PHYSICAL REVIEW VOLUME 168, NUMBER 2 10 APRIL 1968

Itinerant-Electron Theory of Pressure Effects on Ferromagnetic Transition Temperatures: Ni and Ni-Cu Alloys*

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The rate of change of Curie temperature with pressure is calculated for Ni and Ni–Cu alloys by considering the pressure-induced shift of the pole in the uniform static spin susceptibility. The short-range Hamiltonian of Hubbard, Kanamori, and Gutzwiller is employed to describe the interactions among d electrons and, following Kanamori, these interactions are treated in the t approximation. The spin susceptibility is calculated using the Green's-function technique of Martin and Schwinger; the density-of-states curve for paramagnetic Ni computed by Hodges *et al.* is employed in making numerical evaluations. Account is taken of inter-d-band interactions, and of the effect on the number of d holes of changes in the conduction band due to compression. Good agreement with experiment is obtained for Ni. For Ni–Cu alloys, calculations based on the rigid-band model yield poor results; but the use of an almost equally simple model in which a d hole is assumed never to enter a Cu site leads to substantial improvement.

I. PERSPECTIVE COMMENTS

The effects of pressure on magnetic properties in the $3d$ transition metals have been studied experimentally for some years.[1–7] However, theoretical efforts directed at explaining these results using quantum-statistical rather than thermodynamic[8–13] approaches have lagged considerably behind. The basic physical ingredients necessary to a more fundamental theory have not in fact been available until recently, and are, even at the present time, reasonably well established only for metals such as Ni, which have nearly filled $3d$ bands.[14] The most important of these are a Hamiltonian which gives correctly the quasiparticle energy levels of the paramagnetic state and a procedure for describing approximately the interactions among the particles via the Coulomb forces in a way which is both tractable and justifiable, and which, because of the strength of these forces, transcends perturbation theory.

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A suitable model Hamiltonian has been introduced by Hubbard,[15] Kanamori,[16] and Gutzwiller.[17] Correlation effects are regarded in this formulation to be of importance only among the 3*d* electrons, and, because of screening by the conduction electrons, are assumed to be confined to carriers at the same atomic site. In a case such as that of Ni, in which the density of *d* carriers is reasonably small, these interactions may, for arbitrary strengths be treated using the *t* approximation. The single-particle excitation spectrum of the Hamiltonian is taken to be identical to that of a "first-principles" band calculation which, insofar as comparison is possible, provides reasonable agreement with the results of experiment. The validity of a band picture,[18] according to which the *d* electrons are regarded as itinerant, has been amply demonstrated experimentally for Ni.[19–23]

The dependence of the Curie temperature T_C on pressure P is analyzed in this paper[24,25] by studying the pressure-induced shift of the pole in the uniform static spin susceptibility, since this pole marks the second-order phase transition between paramagnetic and ferromagnetic states. This approach to the problem has the great advantage that only the paramagnetic band structure need be considered. In addition to providing an adequate theory of this effect, the present calculations may also be regarded as offering one sort of test of the approximations made in passing from the exact to the model Hamiltonian. For example, according to the *t* approximation, the intra-atomic Coulomb interaction among *d* electrons is replaced by an effective interaction which changes in a definitely specified, albeit complicated manner with volume. A sensitive balance involving this variation, that associated with the density of states of the *d* electrons, and that related to the transfer of electrons between *d* and conduction bands, determines the movement of the pole in the susceptibility. Accordingly, one might expect failures of the *t* approximation and the quasiparticle model to be reflected in values of dT_C/dP which are in gross conflict with experimental results. The incompleteness of this test, however, is evident from the fact that the omission in the present treatment of paramagnon effects,[26,27] which might be expected to play some role, does not appear to spoil the generally good agreement between theory and experiment. Nevertheless, the present test of the model Hamiltonian is more sensitive than that previously given by Hodges *et al.*,[28] who made a band-structure calculation for ferromagnetic Ni in which the effective electron-interaction parameters were considered to be adjustable, and found reasonable values for these parameters upon demanding that the calculation reproduce such experimental features as the observed magneton number. In contrast to the present situation, it was not necessary in that case to assume any specific functional dependence of the effective interactions.

Since the present paper deals with a number of topics, all of which are essential to the development of the theory for the pressure variation of T_C, it may be helpful to provide at this point an overview of the material. Section II gives explicit expressions for the model Hamiltonians, and presents in schematic form a proper derivation of the spin susceptibility in the *t* approximation, using the Martin-Schwinger Green's-function technique[29,30] as described by Baym and Kadanoff,[31] and Fedders and Martin.[32] The treatment (although it leads to almost the same results) is somewhat more complete than that of Herring,[33] which is based on Fermi-liquid theory.[34] Section III considers a particularly simple version of the model Hamiltonian in which the intra-atomic Coulomb forces between electrons in the same orbital are taken to be infinite, and interorbital interactions and effects of the conduction band on the number of *d* carriers are neglected. It is assumed that the *d* band widens uniformly with pressure. Under these circumstances, the entire theory is seen to involve only a single energy parameter, the bandwidth W. Accordingly, one finds on dimensional

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[18] In this connection, it should be noted that the scattering-theoretic approach to transition-metal band structure of Heine (Ref. 41) and Hubbard (Ref. 42), in which the *d* bands and their hybridization with the conduction band are considered to result from the interaction of plane waves with a periodic array of resonant scatterers originating from the atomic *d* levels, is very useful in relating the present model Hamiltonian to others, such as that of Anderson [P. W. Anderson, Phys. Rev. **124**, 41 (1961)], which have been employed in different contexts.

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[32] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).

[33] Reference 14, Chap. 10.

[34] The reader who is willing to accept the resulting expressions for the susceptibility may omit this section and turn to the remainder of the paper.

grounds the extremely simple relation $d \ln T_C = d \ln W$, which is notable in that it is independent of the actual form of the band. A physical discussion based on a rectangular-band model, and an exact analytic treatment (which turns out to be useful in connection with later generalizations), show that dT_C/dP is the sum of largely cancelling contributions due to the increase of the effective electron interaction and the decrease of the density of states with pressure. The consideration of either effect alone permits the establishment of reasonable upper and lower bounds on dT_C/dP (which are respectively positive and negative in sign), and hence of a scale which provides quantitative criteria concerning the extent of agreement between the results of theory and those of experiment. Because this simple theory is independent of the band structure, it can be applied to both Ni and ferromagnetic Ni–Cu alloys, fairly successfully, as it turns out.

Section IV considers a series of generalizations in which the model is made more realistic by including additional physical effects at each stage. It introduces successively finite intra-orbital interactions, the conduction band insofar as it influences the position of the Fermi level, and interactions between different orbitals. Each effect (even that due to the conduction band) is seen to give rise to an appreciable change in the magnitude of dT_C/dP, but the most complicated model, in which all effects are considered together, again provides good agreement with experiment. Since the results now do depend on the model taken for the band structure, the application of the theory to Ni–Cu alloys is no longer so straightforward. The grossly oversimplified rigid-band model,[35] which has been used extensively to describe the simpler properties of these alloys, is seen in Sec. V to predict that the pole in the susceptibility occurs at 0°K for concentrations of Cu much below the experimentally established 57%, and to lead to a qualitatively incorrect dependence on concentration of dT_C/dP (as well as to an electronic specific heat that decreases much too rapidly). Because of these difficulties, an equally simple alternative model is proposed according to which the number of d holes per Ni atom stays constant at all concentrations. The underlying assumption is that each of the two constituents enters the alloy with the atomic configuration characteristic of the pure metal (approximately $3d^9 4s$ for Ni and $3d^{10} 4s$ for Cu). This implies the neutrality, or more precisely "minimum polarity,"[36] of each site, as well as a nearly uniform distribution of conduction electrons over the entire crystal. Use of a particularly simple version of this model is shown largely to eliminate the above-mentioned discrepancies with the results of experiment, but it should be emphasized that the real justification of this description in terms of band theory for nonperiodic systems[37–39] remains to be given.

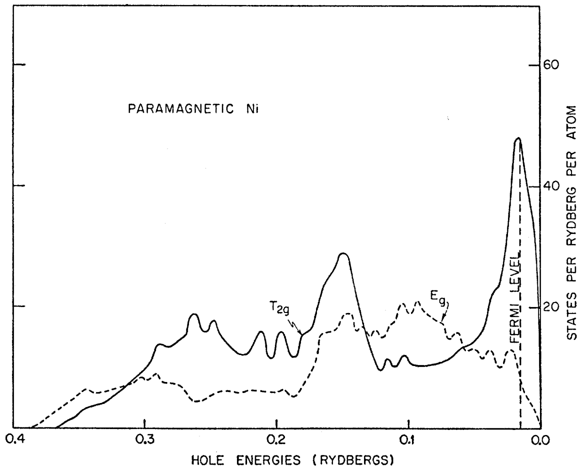

FIG. 1. Contributions of the three t_{2g} and two e_g bands to the density of states of paramagnetic Ni. Origin of energy for holes is taken to be the X_5 level (the top of the electron d band). The state density is assumed to be zero at this point, implying the neglect of hybridization between d and conduction bands in the immediate vicinity.

II. SPIN SUSCEPTIBILITY

This section is devoted to deriving explicit expressions for the uniform static spin susceptibility χ. For this purpose, knowledge of the density-of-states function and the Hamiltonian, as well as of the procedure for treating particle interactions in the t approximation, is necessary. The quantity χ may be obtained from the nonlocal spin susceptibility, which bears a simple relation, via the spin-fluctuation propagator, to an electron-hole correlation function. The latter may be written in terms of the t matrix and the density of states.

A. State Density; Hamiltonian; Use of the t Approximation

This subsection introduces the density of states and Hamiltonian to be employed, and describes the treatment of the latter in terms of the t approximation. The state-density function for paramagnetic Ni will be taken to be that computed by Hodges *et al.*[28,40] using an interpolation scheme, with parameters adjusted to fit the results of an augmented plane wave (APW) calculation. While explicit knowledge of the wave functions is not necessary to this procedure, the assumption of a particular functional form is required in discussing the interaction part of the Hamiltonian. The d-band wave

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[40] L. Hodges, Ph.D. thesis, Harvard University, 1966 (unpublished).

functions are taken to have tight-binding form,[41,42] with the corresponding $3d$ orbitals divided into the t_{2g} group, composed of functions of angular symmetries xy, yz, and zx, and the e_g group, with symmetries x^2-y^2 and $3z^2-r^2$. An examination of the squares of the interpolation-scheme eigenvector components permits a simple separation of the density of states into e_g and t_{2g} (as well as conduction-band) components. This decomposition is shown in Fig. 1.

Even though the Fermi surface of paramagnetic Ni contains a number of electron sheets having mixed d and conduction-band character, it is possible in the present analysis to think of the band structure in somewhat simpler terms. The density of states will always be taken to have its correct form, in which both e_g and t_{2g} contributions, as well as the effects of hybridization with the conduction band, are included. In the calculation of the t matrix, however, this hybridization, except insofar as it changes the state density, will be neglected, as will the relatively small e_g contribution in the case in which interorbital effects are considered explicitly. Under these circumstances, it is valid to regard the d carriers as holes which contain no conduction-band component, and which are located in pockets centered about the points X in the Brillouin zone. In this form, the model represents a slight generalization of that originally proposed by Kanamori[16] and subsequently discussed by Herring.[33]

The simplest case to be considered of the short-range Hamiltonian introduced in Sec. I, referred to hereafter as Case I, will be that in which all interorbital interactions are neglected. In this instance, the Hamiltonian may be written

$$\mathcal{H}=\mathcal{H}_0+\sum_{i\mu} U_\mu n_{i\mu\uparrow}n_{i\mu\downarrow} \qquad \text{(Case I)}, \tag{2.1}$$

where

$$\mathcal{H}_0=\sum_{ij,\mu\mu'\sigma} c_{i\mu\sigma}{}^\dagger c_{j\mu'\sigma}\int d^3r\,\varphi_\mu{}^*(\mathbf{r}-\mathbf{R}_i)\times[-\nabla^2/2m+V(\mathbf{r})]\varphi_{\mu'}(\mathbf{r}-\mathbf{R}_j)$$

with the sums on μ, μ' extending over all (t_{2g} and e_g) orbitals, and with

$$U_\mu=(\mu\mu\,|\,v\,|\,\mu\mu)\,. \tag{2.2}$$

Here $\varphi_\mu(\mathbf{r})$ is an orbital of symmetry μ centered at the origin, $\mathbf{R}_i$ is a lattice vector, $V(\mathbf{r})$ is the periodic potential of the rare-gas cores, and $\hbar$ is taken to be unity. The operator $c_{i\mu\sigma}$ destroys an electron of spin σ at site i in orbital μ; the number operator $n_{i\mu\sigma}$ is defined as $c_{i\mu\sigma}{}^\dagger c_{i\mu\sigma}$. Finally,

$$(\mu_1\mu_2\,|\,v\,|\,\mu_3\mu_4)=\int d^3r\,d^3r'\,\varphi_{\mu_1}{}^*(\mathbf{r})\varphi_{\mu_2}{}^*(\mathbf{r}')v(|\,\mathbf{r}-\mathbf{r}'\,|)\varphi_{\mu_3}(\mathbf{r})\varphi_{\mu_4}(\mathbf{r}'),$$

where $v(|\,\mathbf{r}-\mathbf{r}'\,|)$ is the Coulomb potential.

The second case to be considered, designated Case II, is that in which interorbital interactions are included, but the presence of e_g orbitals is neglected.[16] This approximation is based on the observation already made that the d-hole states in Ni are largely t_{2g} in character. The corresponding Hamiltonian may be written as

$$\begin{aligned}\mathcal{H}=\mathcal{H}_0+U\sum_{i\mu} n_{i\mu\uparrow}n_{i\mu\downarrow}-J\sum_{i,\mu\neq\mu'}\mathbf{S}_{i\mu}\cdot\mathbf{S}_{i\mu'}\\+\tfrac{1}{2}(U'-\tfrac{1}{2}J)\sum_{i,\mu\neq\mu',\sigma\sigma'} n_{i\mu\sigma}n_{i\mu'\sigma'}\\+J'\sum_{i,\mu\neq\mu'} c_{i\mu\downarrow}{}^\dagger c_{i\mu\uparrow}{}^\dagger c_{i\mu'\uparrow}c_{i\mu'\downarrow} \qquad \text{(Case II)},\end{aligned} \tag{2.3}$$

where μ and μ' range only over the three t_{2g} symmetries, and where $\mathbf{S}_{i\mu}$ is the spin operator for electrons in orbital μ on site i. The Coulomb matrix elements involved in Eq. (2.3) are

$$(\mu\mu\,|\,v\,|\,\mu\mu)=U, \tag{2.4a}$$

$$(\mu\mu'\,|\,v\,|\,\mu\mu')=U', \tag{2.4b}$$

$$(\mu\mu'\,|\,v\,|\,\mu'\mu)=J, \tag{2.4c}$$

$$(\mu\mu\,|\,v\,|\,\mu'\mu')=J', \qquad (J'=J)\,. \tag{2.4d}$$

The subscripts μ have been omitted from U, U', J, and J' for convenience, since the three t_{2g} orbitals are equivalent. Equation (2.4a) gives the Coulomb self-energy of an atomic orbital [as does Eq. (2.2)]. The matrix element in Eq. (2.4b) corresponds to a process in which the electrons remain in the original orbitals after scattering (interorbital Coulomb interaction), that in Eq. (2.4c) to one in which they exchange orbitals (Hund's-rule coupling), and that in Eq. (2.4d) to one in which they transfer from one orbital to another[16] (an interaction that is found to be relatively unimportant). The matrix elements of Eqs. (2.4c) and (2.4d) are equal by virtue of the reality of the φ_μ. Possible dependences of the quantities in Eqs. (2.4) on the relative spins of the orbitals are neglected.

Following Kanamori,[16] the particle interactions involved in these Hamiltonians will be treated using the t approximation, which is appropriate for cases in which the density of particles is low and the range of the interaction short. The quantitative criterion for the validity of this approximation is simply that the interaction range a be much smaller than the interparticle distance; i.e., $n^{1/3}a\ll 1$, where n is the particle density. For Ni, $n^{1/3}a\approx 0.3$, which may hardly be characterized as "much less than unity," but which is at least smaller than the value for other transition metals.

The t approximation is most conveniently described in terms of a propagator formalism.[31] The single-particle Green's function $\mathcal{G}(11')\equiv\langle T[\psi(1)\psi^\dagger(1')]\rangle$ represents an extension into the complex time domain of the function $\langle T[\psi_{\sigma_1}(\mathbf{r}_1t_1)\psi_{\sigma_{1'}}{}^\dagger(\mathbf{r}_{1'}t_{1'})]\rangle$. Arguments such as 1 refer to space-time-spin coordinates $(\mathbf{r}_1,\ -i\beta s_1,\ \sigma_1)$, with β the inverse temperature in energy units, and

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[41] V. Heine, Phys. Rev. **153**, 673 (1967).

[42] J. Hubbard, Proc. Phys. Soc. **92**, 921 (1967).

$0 \leq s_1 \leq 1$. In addition, T is Wick's time-ordering operator and

$$\psi_\sigma(\mathbf{r}t) = \exp[i(\mathcal{H}-\mu N)t]\psi_\sigma(\mathbf{r}) \exp[-i(\mathcal{H}-\mu N)t],$$

where μ is the chemical potential, N the total number operator, and $\psi_\sigma(\mathbf{r})$ an operator that destroys a particle of spin σ at the point r. Angular brackets indicate averages over a grand canonical ensemble: $\langle X\rangle = \mathrm{tr}\rho X/\mathrm{tr}\rho$, with $\rho \equiv \exp[-\beta(\mathcal{H}-\mu N)]$.

The integral equation that defines the t matrix is

$$t(13, 1'3') = [\delta(11')\delta(33') - \delta(13')\delta(31')]v(1'3')$$
$$-\beta \int d\bar{1}d\bar{3}\, t(13, \bar{1}\bar{3})\mathcal{G}(\bar{1}1')\mathcal{G}(\bar{3}3')v(1'3'), \quad (2.5)$$

in which use is made of the abbreviations

$$v(12) \equiv v(|\mathbf{r}_1 - \mathbf{r}_2|)\delta(s_1 - s_2),$$
$$\int d1 \equiv \int d^3r_1 \int_0^1 ds_1 \sum_{\sigma 1},$$
$$\delta(12) \equiv \delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(s_1 - s_2)\delta_{\sigma_1\sigma_2}.$$

The t approximation itself consists simply in taking the self-energy function[31] to be

$$\Sigma(11') = \beta \int d\bar{3}d\bar{4}\, t(1\bar{3}, 1'\bar{4})\mathcal{G}(\bar{4}, \bar{3}^+). \quad (2.6)$$

With $\mathcal{G}$, t, and v represented diagrammatically as in Fig. 2(a), Eqs. (2.5) and (2.6) take the forms given in Figs. 2(b) and 2(c).

B. Nonlocal Susceptibility and Particle-Hole Correlation Function

The nonlocal paramagnetic spin susceptibility is given by[43]

$$\chi_{ij}(\mathbf{rr}', \omega) = i \int_0^\infty d(t-t')\, e^{i\omega(t-t')}\langle[M_i(\mathbf{r}t), M_j(\mathbf{r}'t')]\rangle,$$

where M is the magnetization density

$$M_i(\mathbf{r}t) = \mu_B \sum_{\sigma\sigma'} \psi_\sigma^\dagger(\mathbf{r}t)\tau_{\sigma\sigma'}^{(i)}\psi_{\sigma'}(\mathbf{r}t), \quad (2.7)$$

with μ_B the Bohr magneton and $\tau^{(i)}$ the Pauli spin matrices ($i = x$, y, or z). For a cubic crystal, χ_{ij} is proportional to δ_{ij}, and hence only one of the three nonzero elements of the susceptibility tensor, say χ_{zz}, need be considered. Subscripts z will be dropped for convenience.

The nonlocal susceptibility bears a simple relation to the more easily calculated spin-fluctuation propagator $\tilde{\chi}(\mathbf{rr}', t-t') \equiv \langle T[M(\mathbf{r}t)M(\mathbf{r}'t')]\rangle$. Just as in the case of the single-particle Green's function, this propagator can be extended to the imaginary time domain, and written as $\tilde{\chi}(\mathbf{rr}', s-s')$. The Fourier coefficients

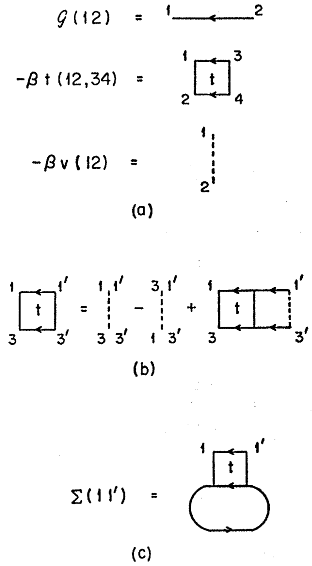

FIG. 2. (a) Diagrammatic representations of the single-particle Green's function, the t matrix, and the Coulomb potential. (b) Integral equation for the t matrix. (c) Self-energy function Σ in t approximation.

are given by

$$\tilde{\chi}(\mathbf{rr}', \omega_\nu) = \int_0^1 ds ds'\, e^{\beta\omega_\nu(s-s')}\tilde{\chi}(\mathbf{rr}', s-s'), \quad (2.8)$$

where $\omega_\nu = \pi\nu/-i\beta$, with ν an even integer. By representing both the nonlocal susceptibility and the spin-fluctuation propagator in terms of spectral densities, it may be seen that

$$\chi(\mathbf{rr}', \omega) = \beta \lim_{\epsilon\to 0+} \lim_{\omega_\nu \to \omega + i\epsilon} \tilde{\chi}(\mathbf{rr}', \omega_\nu). \quad (2.9)$$

The propagator $\tilde{\chi}$ is evaluated by considering its relation to the electron-hole correlation function

$$\mathcal{L}(12, 1'2') = \langle T[\psi(1)\psi^\dagger(1')\psi(2)\psi^\dagger(2')]\rangle$$
$$- \langle T[\psi(1)\psi^\dagger(1')]\rangle\langle T[\psi(2)\psi^\dagger(2')]\rangle$$
$$\equiv \mathcal{G}_2(12, 1'2') - \mathcal{G}(11')\mathcal{G}(22'). \quad (2.10)$$

Using the fact that the single-particle Green's functions have a δ-function dependence on their spin indices, it may be shown, with the help of Eq. (2.7), that

$$\tilde{\chi}(r_1r_2, s_1 - s_2) = \mu_B^2 \sum_{\sigma 1\sigma 2} \tau_{\sigma_1\sigma_1}^{(z)}\tau_{\sigma_2\sigma_2}^{(z)}\mathcal{L}(12, 1^+2^+). \quad (2.11)$$

The integral equation[31,32] for $\mathcal{L}(12, 1'2')$, which may be derived by employing functional-derivative or diagram techniques, is

$$\mathcal{L}(12, 1'2') = -\mathcal{G}(12')\mathcal{G}(21') + \int d\bar{3}d\bar{4}d\bar{5}d\bar{6}\, \mathcal{G}(1\bar{3})\mathcal{G}(\bar{4}1')$$
$$\times \Xi(\bar{3}\bar{5}, \bar{4}\bar{6})\mathcal{L}(\bar{6}2, \bar{5}2'), \quad (2.12)$$

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[43] The approach used here follows that of Fedders and Martin (Ref. 32) and Baym and Kadanoff (Ref. 31).

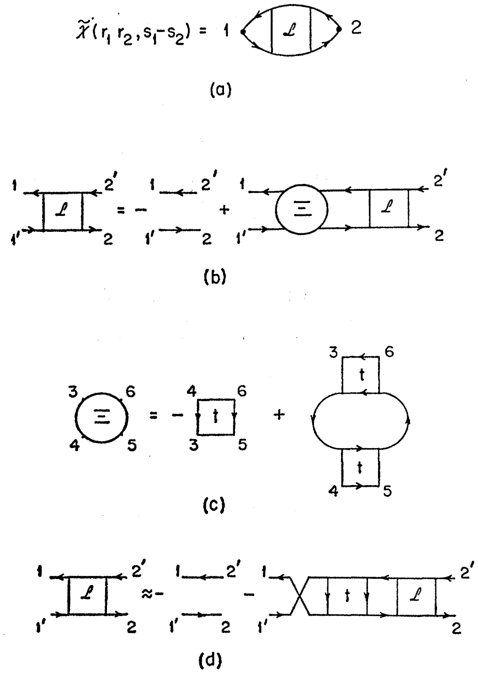

FIG. 3. Diagrammatic representation of equations determining the spin-fluctuation propagator $\tilde{\chi}$ using the t approximation. This quantity is directly related to the spin susceptibility. (a) Connection between $\tilde{\chi}$ and the particle-hole correlation function $\mathcal{L}$. (b) Integral equation for $\mathcal{L}$ in terms of the effective interaction function $\Xi\equiv\delta\Sigma/\delta\mathcal{G}$. (c) Ξ obtained from Fig. 2(c) by taking $\delta/\delta\mathcal{G}$ to correspond to removal of a Green's-function line. (d) Equation for $\mathcal{L}$ in t approximation, omitting term of $O(t^2)$.

where the effective particle-hole interaction Ξ is defined by the relation

$$\Xi(35,46)\equiv\delta\Sigma(34)/\delta\mathcal{G}(65). \qquad (2.13)$$

Equations (2.11) and (2.12) may be represented diagrammatically as in Figs. 3(a) and 3(b). In the former case, the convention is employed of associating $\mu_B\sum_{\sigma_1}\tau_{\sigma_1\sigma_1}^{(z)}$ and $\mu_B\sum_{\sigma_2}\tau_{\sigma_2\sigma_2}^{(z)}$ with the left and right external vertices.

Use of the t approximation for Σ in Eq. (2.13) yields

$$\Xi(35,46)=\beta t(35,46)+O(t^2); \qquad (2.14)$$

the algebraic form of the second term, as well as the details of its derivation, are given in Ref. 31. It will be assumed here and elsewhere that the effective interaction t is small enough so that terms of order t^2 may be neglected. Substitution of this approximation for Ξ into Eq. (2.12) yields the relation

$$\mathcal{L}(12,1'2')=-\mathcal{G}(12')\mathcal{G}(21')+\beta\int d\bar{3}d\bar{4}d\bar{5}d\bar{6}$$
$$\times\mathcal{G}(1\bar{3})\mathcal{G}(\bar{4}1')t(\bar{3}\bar{5},\bar{4}\bar{6})\mathcal{L}(\bar{6}2,\bar{5}2'). \qquad (2.15)$$

The diagrammatic representations of Eqs. (2.14) and (2.15) are given in Figs. 3(c) and 3(d).

C. Solution of the t-Matrix Equation

The solution of Eq. (2.5) will be needed in order to obtain an explicit expression for $\tilde{\chi}$. It will be determined in this subsection by transforming the equation into frequency-momentum space, in a manner roughly parallel to that described by Kanamori[16] and Herring.[33] It is convenient for this purpose to introduce the Bloch function $b_\mu(\mathbf{k},\mathbf{r})$, the solution to the equation

$$[-\nabla^2/2m+\mathcal{V}(\mathbf{r})]b_\mu(\mathbf{k},\mathbf{r})=\epsilon_\mu(\mathbf{k})b_\mu(\mathbf{k},\mathbf{r}).$$

Here $\mathbf{k}$ is the wave vector (assumed to be in the first Brillouin zone), μ the band index, $\epsilon_\mu(\mathbf{k})$ the associated band energy, and $\mathcal{V}$ a one-electron potential obtained in principle by linearizing the Hamiltonian (2.1) or (2.3) in such a way that a quasiparticle spectrum consistent with experiment is obtained.[44] It will be assumed, with Kanamori,[16] that the d-band Bloch functions for hole states may be written as linear combinations of the tight-binding orbitals of only one symmetry type, i.e., that

$$b_\mu(\mathbf{k},\mathbf{r})=N^{-1/2}\sum_i\exp(i\mathbf{k}\cdot\mathbf{R}_i)\phi_\mu(\mathbf{r}-\mathbf{R}_i), \qquad (2.16)$$

with μ equal to xy, yz, zx, x^2-y^2, or $3z^2-r^2$, and with N the number of atoms in the crystal. An examination of the details of the band calculation (and appropriate group-theoretical considerations) indicates that the neglect of mixing of other orbitals into the Bloch eigenfunctions for these states is justified in the case of Ni.

The time transform of the single-particle Green's function is written as

$$\mathcal{G}(\mathbf{r}_1\sigma_1,\mathbf{r}_{1'}\sigma_{1'};\omega_\nu)=\mathcal{G}(\mathbf{r}_1\mathbf{r}_{1'};\omega_\nu)\delta_{\sigma_1\sigma_{1'}}$$
$$=\int_0^1 ds_1ds_{1'}\exp[\beta\omega_\nu(s_1-s_{1'})]\mathcal{G}(11'),$$

where $\omega_\nu=\pi\nu/-i\beta$, with ν an odd integer. In the calculations to be made below, it will be assumed that $\mathcal{G}(\mathbf{r}_1\mathbf{r}_{1'};\omega_\nu)$ may be replaced by the Hartree-Fock single-particle propagator $\mathcal{G}^{\mathrm{HF}}(\mathbf{r}_1\mathbf{r}_{1'};\omega_\nu)$, whose Bloch transform is

$$\mathcal{G}_\mu^{\mathrm{HF}}(\mathbf{k},\omega_\nu)=\int d^3r_1d^3r_1'\,b_\mu^*(\mathbf{k},\mathbf{r}_1)\mathcal{G}^{\mathrm{HF}}(\mathbf{r}_1\mathbf{r}_1';\omega_\nu)b_\mu(\mathbf{k},\mathbf{r}_1')$$
$$=\{\beta[\epsilon_\mu(\mathbf{k})-\epsilon_F-\omega_\nu]\}^{-1}, \qquad (2.17)$$

with ϵ_F the Fermi energy.

It is easily seen that $t(13,1'3')$ may be written in the form

$$t(\mathbf{r}_1\sigma_1,\mathbf{r}_3\sigma_3;\mathbf{r}_{1'}\sigma_{1'},\mathbf{r}_{3'}\sigma_{3'};s_1-s_{1'})\delta(s_1-s_3)\delta(s_{1'}-s_{3'}),$$

and hence the time transform of this function involves

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[44] It should be noted that this potential is not the same as that in $\mathcal{H}_0$. It may be identified with the single-particle potential part of a linearized version of the term $H_{\mathrm{band}}+H_{\mathrm{corr}}^{\mathrm{para}}$ in Eq. (2.8) of Ref. 28.

only the single frequency variable $q_\nu=\pi\nu/-i\beta$, with ν an even integer:

$$t(\mathbf{r}_1\sigma_1,\ \mathbf{r}_3\sigma_3;\ \mathbf{r}_1'\sigma_1',\ \mathbf{r}_3'\sigma_3';\ q_\nu)=\int_0^1 ds_1 ds_{1'}$$

$$\times \exp[\beta q_\nu(s_1-s_{1'})]t(\mathbf{r}_1\sigma_1,\ \mathbf{r}_3\sigma_3;\ \mathbf{r}_{1'}\sigma_{1'},\ \mathbf{r}_{3'}\sigma_{3'};\ s_1-s_{1'}).$$

The Bloch transform of the latter, in turn, is just

$$t(\mu_1\sigma_1\mathbf{k}_1,\ \mu_2\sigma_2\mathbf{k}_2;\ \mu_3\sigma_3\mathbf{k}_3,\ \mu_4\sigma_4\mathbf{k}_4;\ q_\nu)$$

$$=\int d^3r_1d^3r_2d^3r_3d^3r_4\, b_{\mu_1}^*(\mathbf{k}_1,\ \mathbf{r}_1)\, b_{\mu_2}^*(\mathbf{k}_2,\ \mathbf{r}_2)$$

$$\times t(\mathbf{r}_1\sigma_1,\ \mathbf{r}_2\sigma_2;\ \mathbf{r}_3\sigma_3,\ \mathbf{r}_4\sigma_4;\ q_\nu)\, b_{\mu_3}(\mathbf{k}_3,\ \mathbf{r}_3)\, b_{\mu_4}(\mathbf{k}_4,\ \mathbf{r}_4),$$

which is nonzero only when $\mathbf{k}_1+\mathbf{k}_2=\mathbf{k}_3+\mathbf{k}_4+\mathbf{K}$, with $\mathbf{K}$ a reciprocal lattice vector. In spite of the fact that the crystal volume will later be considered a variable, it is taken here to be unity for convenience, since the result of final interest, the criterion for the existence of a pole in the spin susceptibility, does not explicitly involve the volume.

For the Coulomb potential, the Bloch transform is given by

$$\int d^3r_1d^3r_2\, b_{\mu_1}^*(\mathbf{k}_1,\ \mathbf{r}_1)\, b_{\mu_2}^*(\mathbf{k}_2,\ \mathbf{r}_2)$$

$$\times v(|\ \mathbf{r}_1-\mathbf{r}_2\ |)\, b_{\mu_3}(\mathbf{k}_3,\ \mathbf{r}_1)\, b_{\mu_4}(\mathbf{k}_4,\ \mathbf{r}_2),$$

which is seen from Eq. (2.16) to be equal to

$$N^{-1}(\mu_1\mu_2\ |\ v\ |\ \mu_3\mu_4)\,\delta_{\mathrm{k}_1+\mathrm{k}_2,\mathrm{k}_3+\mathrm{k}_4+\mathrm{K}}.$$

Terms that couple different sites have been neglected here, in accordance with the fact that only short-range interactions are included in the Hamiltonians of interest. If the symbol $v(\mu_1\mu_2\mu_3\mu_4)$ is used to represent this expression when $\mathbf{k}_1+\mathbf{k}_2=\mathbf{k}_3+\mathbf{k}_4+\mathbf{K}$, then for Case I,

$$v(\mu\mu\mu\mu)=U_\mu/N, \tag{2.18}$$

where μ may refer either to e_g or t_{2g} bands, and for Case II,

$$\begin{aligned} v(\mu\mu\mu\mu)&=U/N,\\ v(\mu\mu'\mu\mu')&=U'/N,\\ v(\mu\mu'\mu'\mu)=v(\mu\mu\mu'\mu')&=J/N, \end{aligned} \tag{2.19}$$

where μ and μ' refer to t_{2g} bands only, and $\mu\neq\mu'$. Quantities $v(\mu_1\mu_2\mu_3\mu_4)$ other than those listed in each of two cases are zero.

The Fourier transform of Eq. (2.5) may now be written in terms of the total input 4-momentum to the t matrix, $p\equiv(\mathbf{q},\ q_\nu)$ (with ν even), and $\alpha_i\equiv(\mu_i,\ \sigma_i)$, as

$$\begin{aligned} t(\alpha_3\alpha_4\alpha_1\alpha_2;\ p)&=v(\mu_3\mu_4\mu_1\mu_2)\,\delta_{\sigma_1\sigma_3}\delta_{\sigma_2\sigma_4}-v(\mu_4\mu_3\mu_1\mu_2)\,\delta_{\sigma_1\sigma_4}\delta_{\sigma_2\sigma_3}\\ &\quad -N\sum_{\alpha_5\alpha_6} t(\alpha_3\alpha_4\alpha_5\alpha_6;\ p)\,\delta_{\sigma_1\sigma_5}\delta_{\sigma_2\sigma_6}K(\mu_5\mu_6;\ p)\,v(\mu_5\mu_6\mu_1\mu_2). \end{aligned} \tag{2.20}$$

Here

$$\begin{aligned} K(\mu\mu';\ p)&=\beta N^{-1}\sum_{p_1}\mathcal{G}_\mu{}^{\mathrm{HF}}(p_1)\mathcal{G}_{\mu'}{}^{\mathrm{HF}}(p-p_1)\\ &=N^{-1}\sum_{\mathrm{k}}\frac{(1-f_{\mu\mathrm{k}})(1-f_{\mu',\mathrm{q-k}})-f_{\mu\mathrm{k}}f_{\mu',\mathrm{q-k}}}{\epsilon_\mu(\mathbf{k})+\epsilon_{\mu'}(\mathbf{q}-\mathbf{k})-2\epsilon_F-q_\nu}, \end{aligned} \tag{2.21}$$

with $f_{\mu\mathrm{k}}\equiv f(\epsilon_\mu(\mathbf{k}))$ and $f(\epsilon)=[\exp\beta(\epsilon-\epsilon_F)+1]^{-1}$. The fact that the potential matrix elements are momentum-independent in the present approximation implies that the transformed t matrix depends only on p; the argument list of this function may therefore be simplified in the manner indicated here. Umklapp processes have been neglected in obtaining these equations.

If the carriers of interest were electrons, the first term in the numerator of Eq. (2.21) would correspond to intermediate-state propagation of the carriers as an electron-electron pair, while the second would correspond to propagation as a hole-hole pair[45]; if they were holes, as in the present discussion, the meaning of the terms would be reversed. The second term is of higher order in the carrier density than the first,[46] and since the density is considered here to be low, the former term will be neglected. The further approximation will be made of replacing the t matrix everywhere by the real part of its value on the energy shell.

In accordance with the approximations described earlier, it will be assumed that the pair of holes which interact via the t matrix can both be taken to have the wave vector and energy of the same band-edge X_5 state, and that in evaluating Eq. (2.21), μ may be set equal to μ'. These approximations are equivalent to ones described by Herring.[33] The total input wave vector q in Eq. (2.21) is accordingly $2\mathbf{k}^{X_5}$, and so this equation becomes finally (with $\mathbf{k}^X\equiv\mathbf{k}^{X_5}$)

$$\begin{aligned} K_\mu&\equiv N^{-1}\sum_{\mathrm{k}}\frac{(1-f_{\mu\mathrm{k}})(1-f_{\mu,2\mathrm{k}^{\mathrm{X}}-\mathrm{k}})}{\epsilon_\mu(\mathbf{k})+\epsilon_\mu(2\mathbf{k}^X-\mathbf{k})}\\ &=\frac{1}{2}\int_{-\infty}^{\infty}d\epsilon\,\nu_\mu(\epsilon)\{[1-f(\epsilon)]^2/\epsilon\}, \end{aligned} \tag{2.22}$$

where ϵ is the carrier energy measured from the energy of the X_5 state (chosen as the zero) and $\nu_\mu(\epsilon)$ is the density of states per atom per spin direction for band μ. The facts that the above approximations imply $K(\mu\mu';\ p)$ not to be a function of p and to depend on only a single band index have been used to simplify the notation.

Since Eq. (2.20) indicates that

$$t(\alpha_1\alpha_2\alpha_3\alpha_4)=-t(\alpha_1\alpha_2\alpha_4\alpha_3),$$

only one of these two need be mentioned in listing solu-

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[45] D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1962), p. 66.

[46] N. M. Hugenholtz, Physica **23**, 533 (1957).

tions to the equation. The argument p of the t matrix may be omitted in view of the assumptions made above. For Case I, the nonzero solutions of Eq. (2.20) are

$$t(\mu\sigma,\mu\bar{\sigma},\mu\sigma,\mu\bar{\sigma})=\frac{U_\mu/N}{1+U_\mu K_\mu},\qquad(2.23)$$

where $\bar{\sigma}\equiv-\sigma$. For Case II, they are found to be (with $\mu\neq\mu'$)

$$t(\mu\sigma,\mu\bar{\sigma},\mu\sigma,\mu\bar{\sigma})=\frac{U+(U+2J)(U-J)K}{N[1+(U+2J)K][1+(U-J)K]},$$

$$t(\mu\sigma,\mu'\bar{\sigma},\mu\sigma,\mu'\bar{\sigma})=\frac{1}{2N}\left[\frac{U'+J}{1+(U'+J)K}+\frac{U'-J}{1+(U'-J)K}\right],$$

$$t(\mu\sigma,\mu'\sigma,\mu\sigma,\mu'\sigma)=\{(U'-J)/N[1+(U'-J)K]\}.\qquad(2.24)$$

In addition, $t(\mu\sigma,\mu'\bar{\sigma},\mu'\sigma,\mu\bar{\sigma})$ and $t(\mu\sigma,\mu\bar{\sigma},\mu'\sigma,\mu'\bar{\sigma})$ are nonzero; but these are of no particular interest because they do not enter the calculation of the susceptibility. Since only the three equivalent t_{2g} bands are involved, the subscript μ has been omitted from K.

D. Expressions for the Uniform Static Spin Susceptibility

For cases in which the wavelength of the applied field is large compared to a lattice distance (thus permitting averages over a unit cell), it may be shown[47,48] that the macroscopic frequency- and wave-number-dependent susceptibility is

$$\chi(\mathbf{q}\omega)=\int d^3r_1d^3r_2\exp[-i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\chi(\mathbf{r}_1\mathbf{r}_2,\omega).$$

This implies, in conjunction with Eqs. (2.9) and (2.11), that the uniform static spin susceptibility χ is given by the relation

$$\chi=\mu_B{}^2\beta\lim_{p\to0}\sum_{\sigma_1\sigma_2}\tau_{\sigma_1\sigma_1}{}^{(z)}\tau_{\sigma_2\sigma_2}{}^{(z)}$$
$$\times\int d^3r_1d^3r_2\exp[-i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\int_0^1ds_1ds_2$$
$$\times\exp[\beta q_\nu(s_1-s_2)]\mathcal{L}(12,1^+2^+),\qquad(2.25)$$

where

$$\lim_{p\to0}\equiv\lim_{\mathbf{q}\to0}\lim_{\omega\to0}\lim_{\epsilon\to0+}\lim_{q_\nu\to\omega+i\epsilon}.$$

In order to evaluate this expression, it is most convenient to expand the electron-hole correlation function in a Fourier series:

$$\mathcal{L}(12,1'2')$$
$$=\sum_{\mu_1\cdots\mu_4,p_1\cdots p_4}\exp[-\beta(\omega_{\nu_1}s_1+\omega_{\nu_2}s_2-\omega_{\nu_3}s_{1'}-\omega_{\nu_4}s_{2'})]$$
$$\times b_{\mu_1}(\mathbf{k}_1,\mathbf{r}_1)b_{\mu_2}(\mathbf{k}_2,\mathbf{r}_2)b_{\mu_3}{}^*(\mathbf{k}_3,\mathbf{r}_{1'})b_{\mu_4}{}^*(\mathbf{k}_4,\mathbf{r}_{2'})$$
$$\times\mathcal{L}(\mu_1\sigma_1p_1,\mu_2\sigma_2p_2,\mu_3\sigma_{1'}p_3,\mu_4\sigma_{2'}p_4).$$

Here p_j stands for $(\mathbf{k}_j,\omega_{\nu_j})$, where $\omega_{\nu_j}=\pi\nu_j/-i\beta$ (with ν_j an odd integer). If the abbreviation

$$L(\alpha_1\alpha_2\alpha_3\alpha_4)\equiv\lim_{p\to0}\sum_{p_1p_2}\mathcal{L}(\alpha_1p_1,\alpha_2p_2,\alpha_3p_1-p,\alpha_4p_2+p)$$

is introduced, it is seen that

$$\chi=\mu_B{}^2\beta\sum_{\alpha_1\alpha_2}\tau_{\sigma_1\sigma_1}{}^{(z)}\tau_{\sigma_2\sigma_2}{}^{(z)}L(\alpha_1\alpha_2\alpha_1\alpha_2).\qquad(2.26)$$

Fourier analysis of Eq. (2.15) provides a relation that determines L (umklapp processes are neglected):

$$L(\alpha_1\alpha_2\alpha_1\alpha_2)=N\beta^{-1}F_{\mu_1}\delta_{\alpha_1\alpha_2}$$
$$-NF_{\mu_1}\sum_{\alpha_3\alpha_4}t(\alpha_1\alpha_4\alpha_1\alpha_3)L(\alpha_3\alpha_2\alpha_4\alpha_2),\qquad(2.27)$$

where

$$F_\mu=-\beta N^{-1}\lim_{p\to0}\sum_{p_1}\mathcal{G}_\mu{}^{\mathrm{HF}}(p_1)\mathcal{G}_\mu{}^{\mathrm{HF}}(p_1-p)$$
$$=\int_{-\infty}^{\infty}d\epsilon\,\nu_\mu(\epsilon)[\partial f(\epsilon)/\partial\epsilon_{\mathrm{F}}].\qquad(2.28)$$

These last equations may be used to show (easily for Case I, and after some manipulation[25] for Case II) that the uniform static spin susceptibilities are

$$\chi_{\mathrm{I}}=\sum_\mu[2N\mu_B{}^2F_\mu/(1-U_{\mathrm{eff}}{}^\mu F_\mu)],\qquad(2.29)$$

with

$$U_{\mathrm{eff}}{}^\mu\equiv U_\mu/(1+U_\mu K_\mu),\qquad(2.30)$$

and (omitting the unnecessary index μ from F),

$$\chi_{\mathrm{II}}=6N\mu_B{}^2F/[1-(U_{\mathrm{eff}}+2J_{\mathrm{eff}})F],\qquad(2.31)$$

where

$$U_{\mathrm{eff}}\equiv\frac{U+(U+2J)(U-J)K}{[1+(U+2J)K][1+(U-J)K]}$$
$$\approx\frac{U}{1+UK}\qquad(U\gg2J^2K[1+(U+J)K]^{-1})\qquad(2.32)$$

and

$$J_{\mathrm{eff}}\equiv\frac{1}{2}\left[\frac{U'+J}{1+(U'+J)K}-\frac{U'-J}{1+(U'-J)K}\right]$$
$$\approx\frac{J}{(1+U'K)^2}\qquad(U'\gg J).\qquad(2.33)$$

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[47] H. Ehrenreich, in *Proceedings of the International School of Physics "Enrico Fermi," Course 34,* edited by J. Tauc (Academic Press Inc., New York, 1966), p. 106.

[48] S. Adler, Phys. Rev. **126,** 413 (1962).

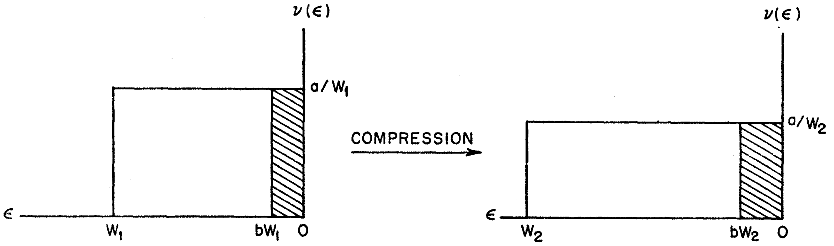

FIG. 4. Uniform widening under compression of the crystal of a hypothetical rectangular band having width W and total number of states a. Each plot gives the density of states versus hole energy; each shaded region shows the fraction b of the band occupied by holes (with Fermi level bW at zero temperature). The parameters a and b do not change with compression.

The approximate expressions for U_{eff} and J_{eff} given here are found generally to be valid for the cases of interest (see Sec. IV).

III. SIMPLIFIED STRONG-CORRELATION MODEL

Under certain restrictive but not too unrealistic assumptions, it is possible to obtain a simple, exact relation connecting the Curie temperature T_C and the crystal volume V. The assumptions are as follows: (1) The quantity U_μ is taken to be infinite, which implies that $U_{\mathrm{eff}}^{\mu}\rightarrow K_\mu^{-1}$. The fact that U_{eff}^{μ} becomes independent of U_μ in this instance, and remains finite, may be interpreted by assuming that for large U_μ, a carrier is excluded from a site already occupied by another of antiparallel spin in the same orbital, and because of the existence of this excluded volume, the kinetic energy of the carrier is increased by an amount $\propto K_\mu^{-1}$. (2) The quantities F_μ and K_μ will be considered to be functionals only of $\nu_\mu(\epsilon)$, and functions only of ϵ_F and β. In particular, they will be taken to have the forms given in Eqs. (2.28) and (2.22). (3) The presence of the conduction band, insofar as it acts to change the number of d holes with compression, will be neglected. (4) The bandwidth W will be assumed to depend only on R, the interatomic distance. Heine's[41] result for the transition metals that $W\propto R^{-5}$, derived using scattering theory, will be employed; this implies that $\zeta\equiv d\ln W/d\ln V=-5/3$.[49] (5) The d band will be taken to widen uniformly when the crystal is compressed. The density of states in each (hole) band will be assumed to have the form

$$\nu_\mu(\epsilon)=\nu_\mu(\epsilon,W)=W^{-1}g_\mu(\epsilon W^{-1}), \qquad (3.1)$$

where g_μ is a function only of ϵW^{-1}. Since the integral over energy of this expression is independent of W, it is clear that in this picture, the number of states in each band remains constant under pressure. Figure 4 shows a rectangular band widening in accordance with Eq. (3.1); the equation may, of course, refer to a band of any shape. Implicit also in taking all state densities to have the above form are the assumptions that e_g and t_{2g} bands widen at the same rate, without changing their relative positions, and that the bottom of the band, taken initially to be the zero of energy, remains the zero. The latter is necessary to accord with the definition of K.

If the sample temperature in the actual experiment is taken to be T_C, then, given these assumptions, it is clear that W and T_C are the only energy parameters in the problem (the Fermi energy may be seen from its definition to depend only on W and $T=T_C$). This implies[50] that

$$d\ln T_C=d\ln W=\zeta d\ln V. \qquad (3.2)$$

In order to see the way in which this result comes about and to exhibit its physical significance, the very simple case of the nondegenerate, rectangular band will be considered, with ϵ_F and K taken to have their zero-temperature forms for simplicity (the band index μ, which takes only one value, is everywhere omitted). The density of states in this instance is given by

$$\nu(\epsilon)=aW^{-1}[\theta(\epsilon W^{-1})-\theta(\epsilon W^{-1}-1)],$$

where θ is the Heaviside step function and a is a constant, in accordance with assumption (5). The behavior of such a band under compression is shown in Fig. 4. In view of assumption (3) and the fact that ϵ_F is evaluated at $T=0$, it is evident that $\epsilon_F=bW$, with b a constant.

The pole in the susceptibility χ_I occurs at the point $U_{\mathrm{eff}}F=1$, with $U_{\mathrm{eff}}=K^{-1}$ by assumption (1). The functions F and K for this special case may be written [cf. assumption (2)]

$$F=-aW^{-1}\int_0^W d\epsilon\,\partial f/\partial\epsilon\equiv W^{-1}S(\beta W), \quad (3.3\mathrm{a})$$

$$K=\tfrac{1}{2}aW^{-1}\int_{bW}^{W}\epsilon^{-1}d\epsilon\equiv cW^{-1}, \qquad (3.3\mathrm{b})$$

where c is a constant. The position of the pole is then

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[49] The recent KKR calculation done by Davis, Faulkner, and Joy for Cu at several different lattice constants (Ref. 57) shows the volume dependence of the over-all d-band width in this metal to be given by $\zeta=-1.62$, in good agreement with the value $-5/3$. If W in the definition of ζ is taken to refer to various energy gaps (such as $\Gamma_{12}-\Gamma_{25}'$) in the d band of this calculation, ζ values that do not deviate from -1.62 by more than a few percent are obtained. This also supports the assumption made below (for Ni) that e_g and t_{2g} bands widen at the same rate under compression, without changing their relative positions.

[50] We are indebted to J. R. Schrieffer for pointing out that this result, obtained in the analytical treatment to be presented below, is for dimensional reasons an immediate consequence of the assumptions listed.

determined by the relation

$$FK^{-1}=c^{-1}S(\beta W)=1,$$

with the corresponding differential condition

$$d(FK^{-1})=c^{-1}dS(\beta W)=0,$$

specifying lines of constant F/K in the V-T plane [W is related to V by assumption (4)]. For $S'(\beta W)\neq 0$, the latter implies that along these lines, $d\beta W=0$, i.e., $d\ln T=d\ln W$. On the particular line determined by $F/K=1$, T is equal to $T_C(V)$, and hence $d\ln T_C=d\ln W$.

At constant temperature, the magnitudes of $U_{\mathrm{eff}}(\rightarrow K^{-1})$ and F in general shift in opposite directions under pressure, since the primary dependences of these quantities are given by $U_{\mathrm{eff}}\sim W$ and $F\sim W^{-1}$ [cf. Eqs. (3.3)]. This fact, and the influence of these shifts on T_C, may be understood in a simple way. Because F is just an effective state density at the Fermi level, it is evident that it should decrease as the band widens with compression. The effect of this is to lower T_C, since spin reversal, and hence ferromagnetism, becomes energetically less favorable. The fact that U_{eff} increases under pressure is seen most readily by using the excluded-volume picture introduced earlier, in which a carrier is considered to be excluded from a site already occupied by another of antiparallel spin, with U_{eff} proportional to the consequent increase of kinetic energy. If it is assumed that the volume of exclusion v, which is determined by the size of the atomic d shell, does not change as the crystal is compressed, then v must become a larger fraction of the total volume available, leading to an enhanced value of U_{eff}. The effect of this is to raise T_C, since U_{eff} characterizes the strength of the interaction tending toward a parallel-spin configuration and hence its increase means that a larger thermal energy is required to disorder the spins.

It might be mentioned that this picture can be analyzed in a crude way to provide an estimate of $d\ln U_{\mathrm{eff}}$. In the free-electron model, an electron occupying a given k state has a kinetic energy $E\propto k^2\propto V^{-2/3}$. Since the interaction strength U_{eff} is proportional to the kinetic energy associated with exclusion of an electron from a volume v,

$$U_{\mathrm{eff}}\propto E(V-v)-E(V)\approx -v\,dE/dV\propto V^{-5/3}.$$

Under compression of the crystal, therefore, $d\ln U_{\mathrm{eff}}=-(5/3)\,d\ln V$, since v is regarded as pressure-independent. This result is coincidentally identical to that which would be obtained from Eq. (3.3b) (taking $U_{\mathrm{eff}}=K^{-1}$ and $\zeta=-5/3$).

It is convenient for purposes of the subsequent development to present a general derivation of Eq. (3.2) based on an examination of the susceptibility expression χ_{I}, with no restrictions except the five made originally. While the dimensional argument given earlier is adequate in the present case, it is no longer valid when other energies, such as U_μ, are present in the problem. The formalism necessary to treat these kinds of situations, which are discussed in Secs. IV and V, represents a simple generalization of the analysis given below.

The poles of χ_{I} are seen, in view of assumption (1), to occur at the points where $F_\mu K_\mu{}^{-1}=1$. It is found numerically that $F_{t_{2g}}$ is much larger than F_{e_g} (subscripts refer to only one band of the given type), while $K_{t_{2g}}$ is approximately equal to K_{e_g}. Thus, as the temperature is lowered in the paramagnetic state, the first pole to occur in χ_{I} is given by $F_{t_{2g}}K_{t_{2g}}{}^{-1}=1$; it is this condition that determines T_C. Succeeding poles are meaningless, since for $T<T_C$ the system is no longer in the ground state for which χ_{I} was originally calculated. The fact that the condition for the first pole seems to imply that the transition takes place in only one group of bands is an artifact produced by assuming a one-to-one orbital-band correspondence and no interorbital interactions.

Since the e_g bands are clearly not of any direct interest (except insofar as they help to determine ϵ_F), the distinguishing subscripts t_{2g} on F and K [as well as on $\nu(\epsilon)$, U, and U_{eff}] will be omitted. The equations implicitly determining $d\ln T_C/d\ln V$ are then

$$F/K=1, \tag{3.4a}$$

$$d\ln F-d\ln K=0. \tag{3.4b}$$

If X is taken to be either F or K, then by assumption (2), $X=X[\nu(\epsilon);\beta,\epsilon_F]$; and hence

$$dX=\int_{-\infty}^{\infty}(\delta X/\delta\nu)_{\beta,\epsilon_F}\delta\nu(\epsilon)\,d\epsilon+X_\beta d\beta+X_\epsilon d\epsilon_F, \tag{3.5}$$

where the subscripts β and ϵ indicate partial derivatives with respect to β and ϵ_F. The differential dX will be computed subject to the requirement that the number of holes be kept constant [cf. assumption (3)], which leads to the elimination of $d\epsilon_F$.

In order to evaluate the first term in Eq. (3.5), an expression for $\delta\nu(\epsilon)$ consistent with assumption (5) is required. Differentiation of Eq. (3.1) leads immediately to the result

$$\delta\nu(\epsilon)=-[\nu(\epsilon)+\epsilon\nu'(\epsilon)]d\ln W, \tag{3.6}$$

from which it follows, for an arbitrary function $Y(\epsilon)$, that

$$\int_{-\infty}^{\infty}Y(\epsilon)\delta\nu(\epsilon)\,d\epsilon=d\ln W\int_{-\infty}^{\infty}d\epsilon\,\nu(\epsilon)\epsilon Y'(\epsilon). \tag{3.7}$$

Account has been taken here of the fact that the d-band density of states is nonzero only over a finite range.

Both F and K may be written in the form

$$X=\int_{-\infty}^{\infty}d\epsilon\,\nu(\epsilon)Z(\epsilon,\epsilon_F,\beta),$$

and therefore, using Eq. (3.7),

$$\int_{-\infty}^{\infty} (\delta X/\delta\nu)_{\beta,\epsilon_F}\delta\nu(\epsilon)\,d\epsilon = d\ln W \int_{-\infty}^{\infty} d\epsilon\,\nu(\epsilon)\epsilon(\partial Z/\partial\epsilon).$$

By adding and subtracting the expression

$$X+\epsilon_F X_\epsilon-\beta X_\beta = \int_{-\infty}^{\infty} d\epsilon\,\nu(\epsilon)[Z+\epsilon_F(\partial Z/\partial\epsilon_F)-\beta(\partial Z/\partial\beta)],$$

this may be recast as

$$\int_{-\infty}^{\infty} (\delta X/\delta\nu)_{\beta,\epsilon_F}\delta\nu(\epsilon)\,d\epsilon = -d\ln W[X+\epsilon_F X_\epsilon-\beta X_\beta] + d\ln W \int_{-\infty}^{\infty} d\epsilon\,\nu(\epsilon) \times[Z+\epsilon_F(\partial Z/\partial\epsilon_F)-\beta(\partial Z/\partial\beta)+\epsilon(\partial Z/\partial\epsilon)]. \quad (3.8)$$

For functions of the general form

$$X=\int_{-\infty}^{\infty} d\epsilon\,\nu(\epsilon)\beta\phi(\beta\epsilon_F,\beta\epsilon), \quad (3.9)$$

the quantity $Z=\beta\phi$ is such that the second term of Eq. (3.8) vanishes. It is clear then, referring to Eq. (3.5), that any X satisfying this requirement, which includes F and K, obeys the differential relation

$$dX=-d\ln W[X+\epsilon_F X_\epsilon-\beta X_\beta]+X_\beta d\beta+X_\epsilon d\epsilon_F. \quad (3.10)$$

In order to discuss the condition that the number of d holes be kept constant, it is necessary to introduce into the analysis the total d-band density of states per atom per spin direction,

$$\tilde{\nu}(\epsilon)\equiv 3\nu(\epsilon)+2\nu_{e_g}(\epsilon)\equiv W^{-1}\tilde{g}(\epsilon W^{-1}), \quad (3.11)$$

in terms of which the number of holes per atom of one spin is

$$N_h=\int_{-\infty}^{\infty} d\epsilon\,\tilde{\nu}(\epsilon)f(\epsilon).$$

It will be convenient to use the definitions $\tilde{F}\equiv\partial N_h/\partial\epsilon_F$ and $\tilde{I}\equiv\partial N_h/\partial\beta$; i.e.,

$$\tilde{F}\equiv\int_{-\infty}^{\infty} d\epsilon\,\tilde{\nu}(\epsilon)\;\partial f/\partial\epsilon_F, \quad (3.12a)$$

$$\tilde{I}\equiv\int_{-\infty}^{\infty} d\epsilon\,\tilde{\nu}(\epsilon)\;\partial f/\partial\beta. \quad (3.12b)$$

The quantity $\tilde{F}$ is the total effective d-band density of states per atom per spin direction at the Fermi level.

It is evident that Eqs. (3.5)–(3.10) apply to functionals X in which $\nu(\epsilon)$ is replaced by $\tilde{\nu}(\epsilon)$. Since $X=\beta N_h$ has the form given by the analog of Eq. (3.9), its differential may be written as in Eq. (3.10). On the other hand, the fact that $dN_h=0$ implies that $d(\beta N_h)=N_h d\beta$. Combining these two expressions for dX leads immediately to the relation

$$d\epsilon_F=(\epsilon_F-\beta\tilde{I}\tilde{F}^{-1})\,d\ln W+\beta\tilde{I}\tilde{F}^{-1}d\ln T. \quad (3.13)$$

If the above form for $d\epsilon_F$ is substituted into Eq. (3.10), it is seen that

$$d\ln X=-(1-\Lambda_X)\,d\ln W-\Lambda_X d\ln T, \quad (3.14)$$

where

$$\Lambda_X=\beta X^{-1}(X_\beta-\tilde{I}\tilde{F}^{-1}X_\epsilon). \quad (3.15)$$

Use of these equations along the lines of constant F/K in the V-T plane defined by Eq. (3.4b) yields

$$-(1-\Lambda_F)\,d\ln W-\Lambda_F d\ln T+(1-\Lambda_K)\,d\ln W +\Lambda_K d\ln T=0. \quad (3.16)$$

The terms $-d\ln W$, which provide the major contributions to $d\ln F$ and $d\ln K$ (see Sec. IV), cancel in this relation, implying that $d\ln T=d\ln W\,(\Lambda_F\neq\Lambda_K)$. For the particular line specified by Eq. (3.4a), T is equal to T_C, and hence Eq. (3.2) follows immediately.

In terms of the abbreviation $\xi\equiv d\ln T_C/d\ln V$, Eq. (3.2) implies simply that $\xi=\zeta$. Both in this section and the ones following, values of ξ must be converted to dT_C/dP values in order to permit comparison with the results of experiment. For this purpose, use may be made of the relation

$$dT_C/dP=-\xi\kappa T_C(1-\xi\alpha T_C)^{-1}, \quad (3.17)$$

obtained under the assumption that the sample is always at T_C. Here $\kappa\equiv-(\partial\ln V/\partial P)_T$ is the compressibility, and $\alpha\equiv(\partial\ln V/\partial T)_P$ the volume thermal-expansion coefficient. In evaluating Eq. (3.17), T_C will be taken to have its experimental value, rather than that which could in principle be obtained by solving the equation for the susceptibility pole.[51] The term $\xi\alpha T_C$ will be neglected in cases in which it introduces a correction $\lesssim 5\%$.

If the value $\zeta=-5/3$ taken for Ni is unchanged as Cu is added, and if the preceding formalism, based on the assumption of a periodic structure, is deemed still to be applicable, then the relation $\xi=\zeta$, in conjunction with Eq. (3.17), may be used to provide an estimate of dT_C/dP for Ni–Cu alloys. It should be noted that the distortion of the density-of-states curve consequent upon alloying is not in itself important: it is required only that the band, whatever its shape, widen uniformly with pressure. The thermal-expansion contribution is not significant in the present case, and hence

$$dT_C/dP\approx(5/3)\kappa T_C. \quad (3.18)$$

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[51] A completely self-contained theory would, of course, begin by calculating U from first principles and then find T_C from the condition $U_{\text{eff}}F=1$. This procedure could in principle be followed here. The reasons for not doing so are given in Sec. IV.

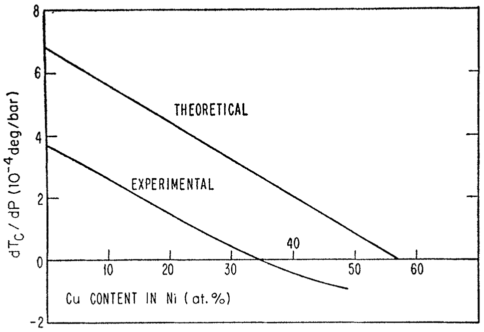

FIG. 5. Comparison for Ni–Cu alloys of dT_C/dP values obtained using the simplified strong-correlation model discussed in the text with those determined by Okamoto *et al.* (Ref. 5).

Ahern, Martin, and Sucksmith[52] have shown experimentally that the Curie temperature of Ni decreases linearly with the addition of Cu at the rate of 11°/at.% Cu, reaching zero at 57 at.% Cu. Thus, if κ is independent of Cu content, Eq. (3.18) predicts a linear decrease of dT_C/dP to zero at this concentration. The value $\kappa = 6.4\times10^{-7}$/bar will be used for both Ni and all Ni–Cu alloy mixtures of interest, in this and succeeding sections.[53] Figure 5 compares the experimental results of Okamoto, Fujii, Tsurui, Fujiwara, and Tatsumoto[5] for Ni–Cu alloys with those obtained from Eq. (3.18). It should be noted that any relation of the form $d\ln T_C/d\ln V = \text{const}$ will, if thermal expansion effects are neglected, lead to a theoretical curve which decreases linearly to zero at the same point as that presented.

In order to assess the quality of the agreement obtained between theory and experiment, it is most convenient to consider only the case of pure Ni. The experimental values for dT_C/dP in Ni show considerable variation, frequently beyond quoted errors (this point is discussed in Ref. 7). In addition to the result 3.7 (units of 10^{-4} deg/bar) found by Okamoto *et al.*, other experimenters give 3.5±0.3 (Ref. 6), 3.2±0.2 (Ref. 2), 3.5±0.2 (Ref. 3), and 4.2±0.7 (Ref. 7); Eq. (3.18) yields the theoretical value 6.8.

Two different theoretical estimates which correspond to reasonable upper and lower limits on dT_C/dP, and which therefore provide a scale on which the above values may be compared, are made as follows: For finite U_μ, the equations that implicitly give $d\ln T_C/d\ln V$ are

$$U_{\text{eff}}F = 1, \tag{3.19a}$$

$$d\ln U_{\text{eff}} + d\ln F = 0. \tag{3.19b}$$

Here, as before, the t_{2g} bands determine the position of the pole in the susceptibility, and so the index μ is again omitted. In computing changes in U_{eff}, it will be assumed that U is independent of V (and T as well). (If U were an interatomic, rather than intra-atomic, matrix element, this assumption would not be justified.) In the Hartree-Fock approximation, $U_{\text{eff}} = U$ is volume-independent. Accordingly, Eq. (3.19b) becomes

$$d\ln F = -(1-\Lambda_F)\zeta d\ln V - \Lambda_F d\ln T_C = 0.$$

Use of Eq. (3.17) (with $\alpha = 5.2\times10^{-5}$/deg)[54] shows dT_C/dP in this instance to be -19×10^{-4} deg/bar, where Λ_F is taken to have the value given in Sec. IV. Just as the case in which U_{eff} is assumed not to change with compression sets a lower limit, that in which F does not vary with compression (but only with temperature) sets an upper limit. It is assumed that the bandwidth is V-independent and that U_{eff} may be viewed solely as an excluded-volume effect in the manner described earlier, implying that $d\ln F = -\Lambda_F d\ln T$ and $d\ln U_{\text{eff}} = -(5/3)d\ln V$.[55] These relations, in conjunction with Eqs. (3.17) and (3.19b), lead to the value $+19\times10^{-4}$ deg/bar for dT_C/dP. Viewed on a scale with limits at $\pm19\times10^{-4}$ deg/bar, the differences between the theoretical and experimental values of dT_C/dP for Ni cited above are not large.

IV. MORE REALISTIC MODELS FOR Ni

In this section, the restrictions previously imposed that U be infinite and that inter-d-band interactions and changes in the number of d holes resulting from pressure-induced conduction-band variations vanish, are removed in stages. Since knowledge of the form of the state-density curve is necessary to evaluate the expressions that arise, it is convenient to examine only the case of Ni here, and to defer consideration of Ni–Cu alloys to Sec. V. The required band-structure-dependent parameters are computed using the density of states of Refs. 28 and 40 for paramagnetic Ni and the experimentally measured value of the Curie temperature; the results of these computations are included in Table I.

The values of dT_C/dP obtained in the various cases analyzed below are given in Table II. The results cluster in a range small compared with that which might

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[52] S. A. Ahern, M. J. C. Martin, and W. Sucksmith, Proc. Roy. Soc. **248A**, 145 (1958).

[53] An estimate of the quantity κ as a function of Cu content, at T just above T_C in every case, may be obtained by correcting the paramagnetic extrapolation of the plot in Ref. 4 of κ versus Cu concentration at room temperature, according to the plot of κ versus T for a given Cu concentration, assuming the latter to be approximately true for all Cu contents and temperatures of interest. The compressibility is seen in this way to decrease from 6.7×10^{-7}/bar for pure Ni to 6.0×10^{-7}/bar for 43 Ni–57 Cu. For simplicity, this variation will be neglected, and κ taken to have the mean value given in the text.

[54] M. P. Arbuzov and M. I. Gitgarts, Fiz. Metal. i Metalloved. **12**, 693 (1961) [English transl.: Phys. Metals Metallog. (USSR) **12**, 61 (1962)].

[55] This simplified physical analysis yields results approximately the same as those which would be obtained from Eq. (3.4b) using $d\ln F = -\Lambda_F d\ln T$ and $d\ln K = -(1-\Lambda_K)\zeta d\ln V - \Lambda_K d\ln T$.

reasonably be expected (-19 to $+19\times10^{-4}$ deg/bar—see Sec. III) because the cancellation discussed earlier of the primary band-widening terms occurs to some degree in all instances. The fact that dT_C/dP may be of either sign has in itself no particular physical significance. Values of the product $U_{\mathrm{eff}}F$, computed at the experimentally measured Curie temperature, are also given in the Table. This product should of course be unity [Eq. (3.19a)]; its deviation from this value is a partial measure of the correctness of the band and interaction-strength parameters used to obtain U_{eff} and F. It should be noted that Eq. (3.19a) is not a useful relation for determining T_C accurately, because $U_{\mathrm{eff}}F$ is a fairly insensitive function of temperature. For example, in Sec. IV D, interaction parameters are so chosen that $I_{\mathrm{eff}}F$ (the analogous product for the case in which inter-d-band interactions are included) is exactly unity at $T=T_C$, but at $T=0$, this product is increased by only 15%. Thus, small errors in F or U_{eff} would lead to large errors in a computed value of T_C.

A. $U\rightarrow\infty$; U', $J=0$; No Conduction-Band Effects

This is the case already considered in Sec. III for which $dT_C/dP=6.8\times10^{-4}$ deg/bar.

TABLE I. Parameters for Ni required in calculating dT_C/dP, evaluated using the paramagnetic state-density curve computed by Hodges *et al.*[a] and the experimentally measured value of T_C.

T_C	633°K
ϵ_F	0.0137 Ry
F	6.64(Ry^{-1}/atom)/spin
F_ϵ	94.8(Ry^{-2}/atom)/spin
F_β	(0.00748/atom)/spin
K	4.90(Ry^{-1}/atom)/spin
K_ϵ	−230(Ry^{-2}/atom)/spin
K_β	(0.00142/atom)/spin
F_c	1.45(Ry^{-1}/atom)/spin
N_c	(0.589/atom)/spin
$\tilde{I}$	−0.000108(Ry/atom)/spin
$\tilde{F}$	23.8(Ry^{-1}/atom)/spin
Λ_F	0.297
Λ_K	0.0191
Λ'_F	0.296
Λ'_K	0.0222
Π_F	0.334
Π_K	−1.10
Ω_F	0.0113
Ω_K	−0.0371

[a] See Refs. 28 and 40.

TABLE II. Values of dT_C/dP and $U_{\mathrm{eff}}F$ computed for Ni.

U (eV)	U' (eV)	J (eV)	Conduction-band effects included?	dT_C/dP (10^{-4} deg/bar)	$U_{\mathrm{eff}}F$ ($I_{\mathrm{eff}}F$ when U', $J\neq0$)
∞	0	0	no	6.8	1.36
5	0	0	no	−1.9	0.87
7.6	0	0	no	0.3	0.99
5	0	0	yes	2.6	0.87
7.6	0	0	yes	5.3	0.99
5	3	1	yes	4.9	1.09
7.6	5	0.6	yes	6.4	1.06
3.9	3	1	yes	3.8	1.00
Hartree-Fock approximation for U_{eff};				−19	···
Excluded-volume picture for U_{eff}; no d-band widening				19	···
Experimental range				3.2–4.2	···

B. $U<\infty$; U', $J=0$; No Conduction-Band Effects

The case to be discussed here is identical to that described above except for removal of the restriction $U\rightarrow\infty$. Effects of inter-d-band interactions and the influence of variations in the conduction band with compression on the number of d holes are neglected. The equations implicitly determining dT_C/dP in this instance are (3.19a) and (3.19b). If

$$R\equiv-d\ln U_{\mathrm{eff}}/d\ln K=UK(1+UK)^{-1}, \qquad (4.1)$$

then Eq. (3.19b) becomes

$$d\ln F-R\,d\ln K=0, \qquad (4.2)$$

assuming U to be independent of V and T. Since $0<U<\infty$ and $K>0$, it is evident that $0<R<1$. Equations (3.14) and (4.2) imply that

$$d\ln T_C/d\ln V=[1-(1-R)(\Lambda_F-R\Lambda_K)^{-1}]\zeta, \qquad (4.3)$$

with the second term vanishing as $U\rightarrow\infty$. If $\Lambda_F-R\Lambda_K=0$, which can be seen from Eq. (3.14) to be equivalent to the condition $\partial(U_{\mathrm{eff}}F)/\partial T=0$ (at $T=T_C$), then $dT_C/dP\rightarrow\pm\infty$. This might produce a cusp in the $T_C(P)$ curve.

There has been considerable dispute[56] as to the size of the parameter U. Its value depends on the role played by processes such as screening by the conduction electrons in the transfer of a d carrier from one atom to another in the solid [the form given in Eq. (2.2) is really an oversimplification]. Herring[33] has estimated that $U\approx5$ eV, and Kanamori,[16] referring to work of Van Vleck,[36] that $U\approx7.6$ eV. Neither writer, it should be noted, considered these values in the context of the case in which interorbital interactions were neglected from the start. Taking U to be 5 eV in Eq. (4.3) implies [in conjunction with Eq. (3.17)] that $dT_C/dP=-1.9\times10^{-4}$ deg/bar; the choice $U=7.6$ eV

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[56] Reference 14, Chap. 9, 10.

yields 0.3×10^{-4} deg/bar. Both of these values of dT_C/dP are somewhat too low.

C. $U<\infty$; U', $J=0$; Conduction-Band Effects Included

In the absence of a conduction band, the Fermi level maintains its relative position within the d band as W increases (temperature effects are neglected for purposes of discussion). This sort of behavior is depicted in Fig. 4. When account is taken of the presence of the conduction band, this simple picture breaks down, since in general compression of the crystal causes carriers to be transferred between d and conduction bands. Two distinct effects produce this transfer. As the lattice constant decreases, the spacing between conduction levels increases, and so if the bottom of the conduction band (marked by Γ_1) were to remain fixed relative to the top of the d band, conduction states would move up through this region, emptying electrons into the d band as they passed through the Fermi level. However, compression leads in fact to a downward movement of Γ_1, which in itself implies a transfer of carriers in the opposite direction. This increase in separation between Γ_1 and the d band has been demonstrated for Cu in the Korringa-Kohn-Rostoker (KKR) calculation of Davis, Faulkner, and Joy, done at different lattice constants,[57] and may be taken to be characteristic of the entire transition series. It occurs because under compression, the mean d-band energy stays roughly constant relative to the atomic zero, while the muffin-tin zero, which gives the approximate position of Γ_1, moves down with respect to this point as the distance between ionic potentials decreases.[58]

It is seen below that of the two opposing mechanisms of carrier transfer, the second is somewhat more important in the present case, and thus changes in the conduction band with compression in themselves cause the Fermi level to move down with respect to X_5. Even though the variations in ϵ_F induced by conduction-band changes are small, they have a substantial effect on the Curie temperature, since the Fermi level lies in a region of steep descent of the $\nu_{t_{2g}}(\epsilon)$ curve near the point $\epsilon=0$ (see Fig. 1), and the thermal distribution of carriers is such that appreciable portions of this region are sampled. Because of this steepness, movement of the Fermi level can be expected to modify significantly the value of $F_{t_{2g}}$, the effective t_{2g} state density at ϵ_F; because of the closeness of ϵ_F to zero, these changes will also have a strong influence on the value of K, since the integral of Eq. (2.22) has an integrand that diverges as $\epsilon\to0$ and an effective lower limit at ϵ_F. It is clear that the downward movement of the Fermi level with pressure increases both F and U_{eff}, and hence raises T_C, in contrast to the widening of the d band, whose effects on these quantities tend not to reinforce but to cancel each other.

In order to obtain forms for $d\ln F$ and $d\ln K$ which include the conduction-band contribution, it is necessary only to modify expression (3.13) for $d\epsilon_F$. For this purpose, it is convenient to designate hole energies, with the zero taken at the top of the electron d band, by the letter ϵ (as before), and electron energies, with the zero set at a fixed distance from $\epsilon=0$, by the letter E (see Fig. 6). The quantity $d\epsilon_F$ is then determined by the requirement

$$\int_{-\infty}^{\infty} d\epsilon\,\tilde{\nu}(\epsilon)[1-f(\epsilon)]+\int_{-\infty}^{\infty} dE\,\nu_c(E)f(E)=\text{const},$$

where $\nu_c(E)$ is the conduction-band-state density per atom for one spin direction. With the definitions

$$N_c\equiv\int_{-\infty}^{\infty} dE\,\nu_c(E)f(E),\tag{4.4}$$

where N_c is the number of conduction electrons per atom of one spin,

$$\delta N_c\equiv\int_{-\infty}^{\infty} f(E)\,\delta\nu_c(E)\,dE$$

and

$$F_c\equiv\int_{-\infty}^{\infty} dE\,\nu_c(E)\,\partial f/\partial E_F,\tag{4.5}$$

it is seen that

$$d\epsilon_F=(\tilde{F}+F_c)^{-1}\delta N_c+\frac{\epsilon_F\tilde{F}-\beta\tilde{I}}{\tilde{F}+F_c}\,d\ln W+\beta\,\frac{\tilde{I}-I_c}{\tilde{F}+F_c}\,d\ln T.\tag{4.6}$$

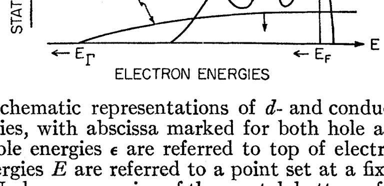

FIG. 6. Schematic representations of d- and conduction-band-state densities, with abscissa marked for both hole and electron energies. Hole energies ϵ are referred to top of electron d band; electron energies E are referred to a point set at a fixed distance from $\epsilon=0$. Under compression of the crystal, bottom of conduction band (at E_Γ) moves down, while conduction-band-state density decreases. These two effects tend to move the Fermi level in opposite directions; net result is found to be a lowering of the Fermi energy E_F.

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[57] H. L. Davis, J. S. Faulkner, and H. W. Joy, Phys. Rev. (to be published). We are grateful to Dr. Davis for sending us a preliminary report of this work.

[58] The implications of this point are currently being developed in collaboration with R. E. Watson. See also J. M. Ziman, Proc. Phys. Soc. (London) **91**, 701 (1967).

The quantity

$$I_c \equiv \int_{-\infty}^{\infty} dE\, \nu_c(E)\,\partial f/\partial\beta$$

is found numerically to be very small, and will be neglected. If X is taken to be either F or K, and the definition

$$\eta \equiv (\partial \ln N_c/\partial \ln V)_{\beta,E_F}$$

is introduced, then it may be shown that

$$d\ln X = [-(1-\Lambda_X'+\Omega_X)\zeta + \Pi_X\eta]\,d\ln V - \Lambda_X'\,d\ln T, \tag{4.7}$$

where

$$\Lambda_X' \equiv \beta X^{-1}[X_\beta - X_\epsilon \tilde{I}/(\tilde{F}+F_c)], \tag{4.8}$$

$$\Omega_X \equiv X_\epsilon F_{c\epsilon_F}/X(\tilde{F}+F_c), \tag{4.9}$$

and

$$\Pi_X \equiv X_\epsilon N_c/X(\tilde{F}+F_c). \tag{4.10}$$

[The function $\nu_c(E)$ has been taken to be independent of E_F and β.]

In this part of the analysis, hybridization effects between d and conduction bands are neglected to lowest order. The conduction band is regarded as essentially free-electron-like over the energy range of interest, with the higher plane waves having a relatively small influence on the values of the integrals that appear and on their volume dependence. Results for F_c and N_c computed using the free-electron model are included in Table I. Since

$$\nu_c(E) \propto V(E-E_\Gamma)^{1/2}\theta(E-E_\Gamma)$$

in this model, with E_Γ the energy of the Γ_1 level, it is seen from Eq. (4.4) that

$$\eta = 1-(F_c/N_c)\,dE_\Gamma/d\ln V. \tag{4.11}$$

For Cu, it was found by Davis *et al.*[57] that

$$dE_\Gamma/d\ln V = 0.55 \text{ Ry}.$$

Assuming this value to be correct also for Ni leads to the result $\eta = -0.36$. The fact that $\eta < 0$ shows the downward movement of E_Γ under pressure to outweigh the decrease of $\nu_c(E)$ in determining $d\epsilon_F$.

From Eqs. (4.2) and (4.7), it may be seen that

$$\frac{d\ln T_C}{d\ln V} = \left[1-\frac{1-R}{\Lambda_F'-R\Lambda_K'}\right]\zeta - \left[\frac{\Omega_F-R\Omega_K}{\Lambda_F'-R\Lambda_K'}\right]\zeta + \left[\frac{\Pi_F-R\Pi_K}{\Lambda_F'-R\Lambda_K'}\right]\eta$$

$$\equiv \xi_1+\xi_2+\xi_3. \tag{4.12}$$

The presence of the term ξ_1 in this equation is due solely to widening of the d band: it would appear even if the conduction band were absent (with Λ_X' replaced by the numerically nearly identical Λ_X). The term ξ_3 describes the effect of changes in the conduction band on the relative location of the Fermi level within the d band, while ξ_2 arises from the fact that even if, as the lattice is compressed, the conduction band were to stay fixed in position without changing its state density (i.e., $\eta = 0$), there would still be a transfer of carriers between it and the d band.

Evaluations of the ξ_i may be made using the U values 5 eV and 7.6 eV discussed earlier, and the sums $\sum \xi_i$ converted to dT_C/dP values term by term (since thermal expansion effects, which introduce a nonlinearity into the relation between dT_C/dP and $d\ln T_C/d\ln V$, are small enough to be neglected in the present case). The results are

$$dT_C/dP = -1.9-0.9+5.4 = 2.6 \qquad (U = 5 \text{ eV})$$

$$= 0.3-0.9+5.9 = 5.3 \qquad (U = 7.6 \text{ eV}).$$

Units of 10^{-4} deg/bar are employed here, and terms are placed in the same order as that of Eq. (4.12). The third term is comparable to the first because, as noted above, compression-induced conduction-band effects on U_{eff} and F tend to reinforce each other in determining dT_C, while the effects of d-band widening tend largely to cancel. The second term does not represent a physically important process, and need not be considered in any detail.

D. $U < \infty$; U', $J \neq 0$; Conduction-Band Effects Included

The effects of inter-d-band interactions will now be introduced, completing removal of the restrictions discussed at the beginning of the section. This is done simply by replacing the expression for χ_{I} in the preceding discussion by that for χ_{II} [Eq. (2.31)]. The equations which now implicitly determine $d\ln T_C/d\ln V$ are

$$I_{\text{eff}}F = 1, \tag{4.13a}$$

$$d\ln I_{\text{eff}} + d\ln F = 0, \tag{4.13b}$$

where $I_{\text{eff}} \equiv U_{\text{eff}} + 2J_{\text{eff}}$. It is convenient here to redefine R as $-d\ln I_{\text{eff}}/d\ln K$. With this definition, Eq. (4.13b) leads to a relation identical to that of Eq. (4.2) (assuming U, U', and J to be independent of V and T), which implies that the equations of Sec. IV C may be applied to the present case.

The fact that J is reduced by the square of $(1+U'K)$ [Eq. (2.33)], rather than by the first power, means that J_{eff} is a relatively more sensitive function of pressure than U_{eff}, and hence that the inclusion of interband interactions will in general enhance the value of R. It is found in the present calculation that the numerically most important result of this enhancement is to reduce the numerator $1-R$ in term ξ_1 of Eq. (4.12), which decreases the value of this term, and hence increases the computed result for dT_C/dP.

In addition to his estimate that $U = 5$ eV, Herring

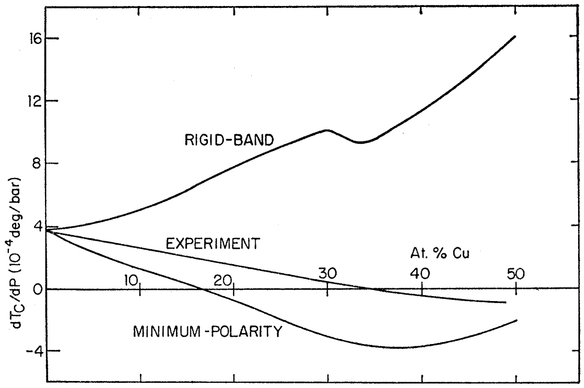

FIG. 7. Comparison for Ni–Cu alloys of dT_C/dP values determined experimentally by Okamoto *et al.* (Ref. 5) with those computed using the rigid-band and minimum-polarity models.

takes $U'=3$ eV and $J=1$ eV.[33] These values are found to give $dT_C/dP=4.9\times10^{-4}$ deg/bar. Kanamori assumes U to be 7.6 eV and J to be 0.6 eV,[16] but makes no numerical estimate of U'. Taking it to be 5 eV in this instance yields 6.4×10^{-4} deg/bar for dT_C/dP. Neither of these sets of values for U, U', and J leads to results satisfying Eq. (4.13a) at the experimentally measured Curie temperature (see Table II). It is of course possible to find an arbitrarily large number of such sets of values for which the product $I_{\text{eff}}F$ is exactly unity at this temperature. If, for example, U' and J are taken to be 3 eV and 1 eV as assumed by Herring, then the choice $U=3.9$ eV completes such a set. These particular values for the interaction parameters lead to the result $dT_C/dP=3.8\times10^{-4}$ deg/bar.

V. Ni-Cu ALLOYS

In Sec. III, a simplified strong-correlation analysis was applied not only to Ni but to Ni–Cu alloys as well. The use in the Ni–Cu case of a formalism based on the t approximation would seem in fact, apart from effects of disorder, to be more justified than its application to pure Ni, since insofar as the additional electrons associated with Cu atoms tend to fill the d band, the assumption of low carrier density should have greater validity. In order to apply the more realistic treatment of Sec. IV to Ni–Cu alloys, it is necessary to have a model for this system which permits computation of the various band-structure-dependent quantities involved. One widely used picture, in which filling of the d band is in fact the sole effect, is the rigid-band model, introduced by Mott[35] in 1935. It is assumed in this model that the density of states of a given pure crystal remains unchanged as another component is added to form an alloy. The electrons are considered to be distributed equally among both types of sites, and thus the only significant effect of alloying is to change the position of the Fermi level. In Ni, there is about 0.6 of an unfilled state below the top of the d band (X_5), and so this band should be just completely filled when the concentration of Cu (which has one additional electron per atom) reaches 60 at.%. The fact that both the Curie temperature and magnetization in the Ni–Cu system are found experimentally to vanish at about this concentration[52] has been taken to support the rigid-band hypothesis for these alloys. An examination of other effects, however, particularly the pressure dependence of the Curie temperature, shows the model to be seriously at fault. Figure 7 indicates that dT_C/dP calculated using the rigid-band description exhibits a qualitatively incorrect dependence on Cu concentration, its magnitude showing an increase rather than the decrease which is experimentally observed. The analysis of Sec. III could not reveal such a failure because, as emphasized there, the results were independent of the explicit form of the density-of-states function. In addition, it will be seen in the following discussion that the criterion for the existence of ferromagnetism in these alloys is violated at Cu concentrations far lower than those for which the alloy is known to be ferromagnetic. Finally, the computed density of states at the Fermi level in ferromagnetic Ni–Cu alloys (the only instance in this paper in which parameters of the ferromagnetic state are considered) decreases much too rapidly in comparison with the observed electronic specific-heat coefficient as the concentration of Cu increases.

In order to help resolve these discrepancies with the results of experiment, a simple alternative model, based on the recognition that the rigid-band model is deficient in failing to take into account the repulsive interaction between d holes and Cu atoms, will be proposed.[59] It will be assumed that in Ni–Cu alloys, the two constituents retain the atomic configurations characteristic of the pure crystals: approximately[60] $3d^94s$ and $3d^{10}4s$. As a consequence, each site remains neutral, and the concentration of conduction electrons stays roughly constant over the entire solid. This assumption undoubtedly represents an oversimplification, since there is probably at least some charge transfer between Ni and Cu sites. It should be emphasized in this connection that by contrast, the rigid-band hypothesis constrains each site to have an appreciable ionic character. The proposed model is the simplest of a class of what might be called "minimum-polarity" models, recalling the use of this term by Van Vleck in describing correlations among the d electrons in transition metals.[36] It will be seen to yield considerably more satisfactory agreement with experiment than that obtained using the rigid-band model in the three instances mentioned above.

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[59] Since the completion of this work, W. M. Lomer has kindly informed us that a similar model was introduced by J. H. O. Varley, Phil. Mag. **45**, 887 (1954), to account for the heats of formation of binary alloys.

[60] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

In quantitative terms, the difference between the two models may be stated as follows: Whereas in the rigid-band picture, the number of d holes per atom in Ni–Cu alloys is $0.6-x$ for $x<0.6$ and zero for $x>0.6$ (with x the atomic Cu concentration), the minimum-polarity hypothesis (in the simple form employed here) implies that this number is $1-x$, since a d hole is considered never to enter a Cu site. Because the portion of the density-of-states curve that is of primary interest lies in the energy region about E_F, the Cu d band, which undoubtedly appears as a virtual level below this region, will be ignored in discussing the minimum-polarity model. The additional assumption will be made that per Ni atom, the paramagnetic d-band state density remains unchanged as Cu is added, implying that the density for the alloy may be written

$$\tilde{\nu}_{\mathrm{Ni-Cu}}(\epsilon)=(1-x)\tilde{\nu}_{\mathrm{Ni}}(\epsilon),$$

with a similar relation for t_{2g} states alone. The assumption that the d band does not narrow appreciably with alloying, contrary to the behavior which might be characteristic of a virtual-crystal model, may not be unreasonable for low Cu concentrations, since statistical clustering of Ni atoms is expected to replace the sharp d-band edges of the pure crystal by appreciably broadened tails.

The analysis of Sec. IV may now be immediately applied to the Ni–Cu case, using the rigid-band and minimum-polarity descriptions of these alloys, and the set of values $U=3.9$ eV, $U'=3$ eV, and $J=1$ eV introduced at the end of Sec. IV. It is convenient for purposes of discussion to write Eq. (4.12) in the approximate form

$$d\ln T_C/d\ln V\approx -5/3+(5/3)(1+UK)^{-1}(\Lambda_F'-R\Lambda_K')^{-1}+\xi_2+\xi_3. \quad (5.1)$$

The two initial terms in this equation correspond to that denoted ξ_1 in Eq. (4.12). The first of these gives $d\ln T_C/d\ln V$ in the strong-correlation limit, with inter-d-band and conduction-band effects neglected, while the second represents, in approximate form (exact when $U', J=0$) the correction arising when U is taken to be finite. The ξ_2 term is never of primary importance, and need not be discussed further, while ξ_3 is found to be roughly the same for the two models under consideration.[25] It is, therefore, the second term that is responsible for the sharp differences in the behavior of the two computed dT_C/dP curves shown in Fig. 7.

From Fig. 8 it is seen that $\Lambda_F'-R\Lambda_K'$ decreases with x in roughly the same way for both rigid-band and minimum-polarity models. The quantity K, however, and hence $(1+UK)^{-1}$, changes in exactly opposite ways in the two instances (Fig. 8). In the rigid-band case, the increase of $1+UK$ is sufficiently rapid largely to compensate the decrease in $\Lambda_F'-R\Lambda_K'$, and as a result, the second term of the above equation is found always to be subordinate in importance to the conduction-band term ξ_3, a strongly negative quantity whose magnitude increases with x. The associated dT_C/dP $(\approx -\kappa T_C d\ln T_C/d\ln V)$, therefore, rises with increasing Cu concentration, in contrast to the behavior found experimentally. In the minimum-polarity case, on the other hand, the decrease of $\Lambda_F'-R\Lambda_K'$ is reinforced by that of $1+UK$, and thus the second term in Eq. (5.1) becomes more and more positive as the level of Cu concentration is raised. This increase is found largely to counterbalance the decrease of ξ_3, and good agreement is obtained with the results of experiment (Fig. 7).

It is possible to give a simple physical interpretation for the difference in behavior of K in the two models which leads to such a dissimilarity in the results for dT_C/dP. The higher the Cu concentration in the rigid-band case, the smaller the number of d holes, and hence the more easily they avoid each other. For this reason K, whose magnitude determines the effectiveness of this correlation [cf. Eqs. (2.32) and (2.33)], increases with x. In the minimum-polarity model, on the other hand, Cu sites are completely unavailable to d holes, and thus this avoidance becomes more difficult as Cu is added, implying a decrease of K with x.

A second failure of the rigid-band model is its inability to satisfy properly the criterion for the occurrence of a phase transition [Eq. (4.13a)], a deficiency alluded to by Kanamori.[16] According to the rigid-band model, I_{eff} decreases as Cu is added, since K increases. In addition, because ϵ_F moves toward a region of lower state density (see Fig. 1), F decreases as well. Thus, for a sufficiently large Cu concentration, though one short of the approximately 60% which would just fill the d band, it must be impossible to satisfy Eq. (4.13a) at any temperature.[61] Kirkpatrick in fact has found, using the above procedures, that this relation implies T_C to be zero at only 10% Cu.[62] Figure 9 shows $I_{\mathrm{eff}}F$ at the experimental value of the Curie temperature (as a function of x), evaluated for the rigid-band model. A correct theory of course would yield a horizontal curve of ordinate unity.

The minimum-polarity model, on the other hand, yields an $\mathrm{I}_{\mathrm{eff}}$ that increases with x (since $K\downarrow$). This means that though F is found to decrease here even a little more rapidly as Cu is added than it did in the rigid-band case,[25] the product $I_{\mathrm{eff}}F$ computed at the experimental Curie temperature remains closer to unity (Fig. 9). The value of T_C implicitly determined by Eq. (4.13a) for this model decreases to zero at about 35% Cu,[62] which represents a decided improvement over the rigid-band result.

It is instructive finally to examine the way in which the minimum-polarity model improves the agreement

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[61] It should again be noted that paramagnon effects have not been included in the present treatment.

[62] E. S. Kirkpatrick (unpublished).

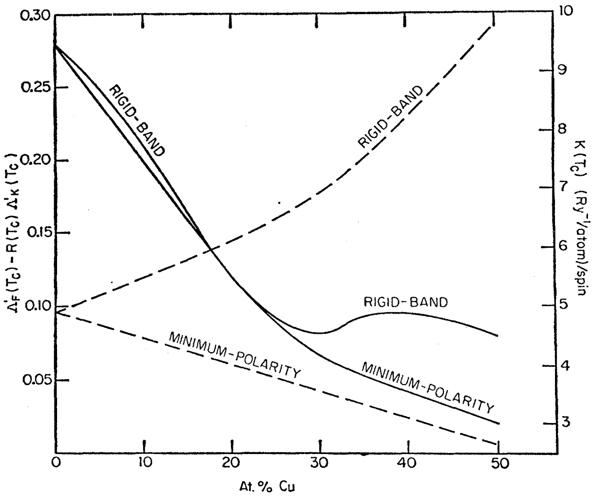

FIG. 8. The quantities $\Lambda_F' - R\Lambda_K'$ (solid lines) and K (dashed lines) for Ni–Cu alloys, evaluated at the experimentally measured Curie temperatures using the rigid-band and minimum-polarity models. It is the difference in behavior of the two K curves that leads to the dissimilarity of the computed results for dT_C/dP shown in Fig. 7.

with the results of low-temperature specific-heat experiments. Figure 10 compares, as functions of x, the electronic specific-heat coefficients for Ni–Cu alloys, measured by Gupta, Cheng, and Beck,[63] with the zero-temperature Fermi-level state densities computed for these alloys using the rigid-band and minimum-polarity models. All curves in the figure are normalized to the same value at $x=0$. In graphing the specific-heat results, the proportional contribution of dressing effects was assumed to be independent of x. The curve for the rigid-band case was obtained using the density of states for the minority-spin band of ferromagnetic Ni calculated by Hodges *et al.*[28,40] The fact that in these calculations the state-density peak near the top of each spin band is higher in the ferromagnetic than the paramagnetic case was taken into account by scaling the peak height linearly between $x=0$ and $x=0.6$. The curve rises initially because the Fermi level is on the ascending rather than the descending side of this peak in ferromagnetic Ni. For the minimum-polarity case, the contributions of both minority- and majority-spin bands must be included. The effects of the concentration dependence of the splitting between these bands in the ferromagnetic region were incorporated in an approximate way,[64] and the peak heights were scaled as before. The experimental curve in Fig. 10 strongly suggests that d holes are present even at large Cu concentrations. This fact stands in sharp disagreement with the predictions of the rigid-band picture, but accords well with those of the minimum-polarity model. It should be emphasized in conclusion that while a formal theory for this model (and the associated refinements) remains to be given, the fact that it is able to account in a reasonable way for a variety of experimental results shows it to be worthy of further consideration.

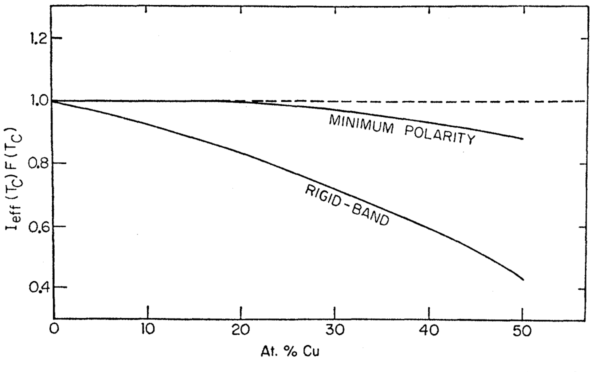

FIG. 9. The product $I_{\rm eff}F$ for Ni–Cu alloys, computed at the experimentally measured Curie temperatures using the rigid-band and minimum-polarity models. Its value should be unity at all Cu concentrations for which the mixture is ferromagnetic (dashed line).

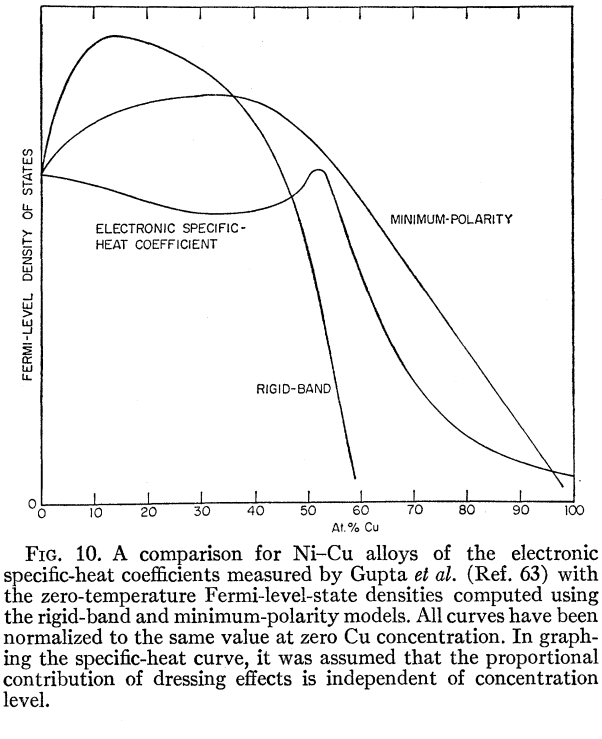

FIG. 10. A comparison for Ni–Cu alloys of the electronic specific-heat coefficients measured by Gupta *et al.* (Ref. 63) with the zero-temperature Fermi-level-state densities computed using the rigid-band and minimum-polarity models. All curves have been normalized to the same value at zero Cu concentration. In graphing the specific-heat curve, it was assumed that the proportional contribution of dressing effects is independent of concentration level.

ACKNOWLEDGMENTS

We are grateful to P. C. Martin for a number of useful conversations concerning Sec. II. Helpful comments from A. R. Williams and E. Asher are also very much appreciated.

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[63] K. P. Gupta, C. H. Cheng, and P. A. Beck, Phys. Rev. **133**, A203 (1964).

[64] The splitting was decreased to zero at $x=0.6$ in such a way as to change the number of electrons in each spin band linearly with x.