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Effect of impurities on the magnetic ordering in chromium

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It is well known that impurities profoundly alter the magnetic properties of chromium. For example, doping with as little as 0.2% vanadium changes the phase transition from weakly first order in pure chromium to second order. While vanadium impurities suppress the Néel temperature T_N, doping with manganese dramatically enhances T_N. Impurities also change the wave vector of the spin-density wave, which has the order parameter g. According to the theory of Young and Sokoloff (YS), the first-order transition in pure chromium is caused by a charge-density wave with order parameter $\delta \propto g^2$. Scattering by impurities suppresses the charge-density wave and drives the transition to second order. In this paper we refine the YS formalism by examining the subtle balance between the spin-density and charge-density terms in the free energy. We find that the first-order transition is destroyed when the concentration of vanadium exceeds about 0.15%, in agreement with experimental measurements. We also study the effect of impurities on the band structure and Néel temperature.

I. INTRODUCTION

As shown by neutron-scattering[1,2] and elastic-strain[3,4] measurements, the antiferromagnetic phase transition of chromium at $T_N \approx 310$ K is weakly first order. Below T_N the spin-density wave[5] (SDW) in chromium is incommensurate with the lattice.[6,7] The profound effect of impurities on the magnetic ordering in chromium has puzzled and intrigued scientists for some time. Doping with as little as 0.2% vanadium destroys the first-order transition, and doping with 0.1% manganese broadens the transition so that its order is indeterminate.[3] While doping with vanadium decreases the Néel temperature T_N, doping with manganese increases T_N substantially.[6] The mean-field theories developed by Zittartz[8] and Young and Sokoloff[9] (YS) do indeed predict that impurities will suppress the first-order transition and shift the Néel temperature. By examining the subtle balance between competing terms in the free energy, we find that the YS theory can produce a threshold concentration of impurities below 0.2% and can explain the effects of vanadium and manganese impurities on the Néel temperature.

The band structure of pure chromium[10] is composed of an electron "jack" and a slightly larger hole "octahedron," which are imperfectly nested by the wave vector $Q = 2\pi(1+\partial)/a$, where a is the lattice constant of chromium. Because $\partial < 0$, the SDW with wave vector Q is incommensurate with the lattice. The addition of vanadium, with fewer conduction electrons than chromium, lowers the Fermi energy of the system, thereby enlarging the hole octahedron and reducing the electron jack.[6] Therefore doping with vanadium increases the magnitude of the mismatch ∂ and the incommensurability of the SDW. But alloying with manganese or rhenium, which have more conduction electrons than chromium, decreases the mismatch $|\partial|$ and increases the commensurability of the SDW.

Because $Q \neq 2\pi/a$, the band structure of chromium actually contains one electron and two hole surfaces,[5] as shown in Fig. 1(a). Because of the coupling between the hole surfaces, even harmonics of the SDW may exist. The second harmonic of the SDW is equivalent to a charge-density wave (CDW) with wave vector $2Q$.

While the SDW is induced by the Coulomb interaction λ between the electron and hole surfaces,[9] the CDW is induced by the Coulomb interaction λ' between the two hole surfaces. As we shall see, the CDW order parameter δ is proportional to the square of the SDW order parameter g. So, near T_N, δ is usually quite small. But a CDW instability occurs as the Coulomb interaction λ' approaches $\frac{1}{2}$. When $\lambda' = \frac{1}{2}$ the CDW may exist even if $g = 0$.

According to the mean-field theory of YS, the CDW is responsible for the first-order transition in pure chromi-

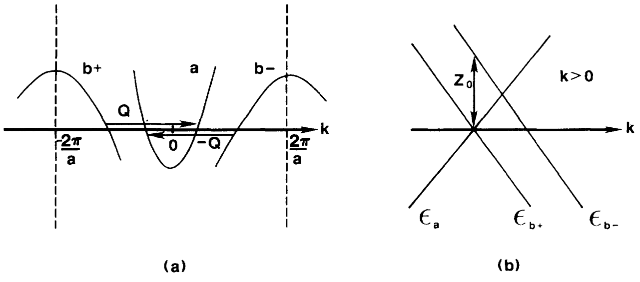

FIG. 1. Schematic drawing of the two hole and one electron bands in chromium, which are imperfectly nested by the wave vector Q. The energy levels near the Fermi surface are also shown for $k > 0$.

um. When λ' is sufficiently close to $\frac{1}{2}$, the large CDW drives the first-order transition. The threshold value of λ', above which the transition becomes first order, is given by λ'_F. So the phase transition is first order in the regime $\lambda'_F < \lambda' < \frac{1}{2}$; above $\frac{1}{2}$ or below λ'_F, the transition is second order. Because the transition is weakly first order, λ' is just above the threshold value $\lambda'_F \approx 0.4$.

Although weak, the first-order transition in pure chromium was clearly observed by Arrott, Werner, and Kendirick,[1] who measured a discontinuous change at T_N in the neutron-scattering intensity at the wave vector $\mathbf{Q}$. Arrott, Werner, and Kendirick found that the rms magnetic moment of the SDW at T_N is about 0.27 times the magnetic moment at $T=0$. The first-order transition can also be observed in the discontinuous change of the linear strain and thermal expansivity[3,4] of pure chromium at T_N.

Adding impurities to a sample of pure chromium quickly destroys the weak first-order transition. A sample with 0.2% vanadium no longer displays a discontinuity in the neutron-scattering intensity[2] at $\mathbf{Q}$. The discontinuity in the thermal expansivity is smaller[3] in a sample with 0.1% vanadium and vanishes in a sample with 0.2% vanadium. In neutron-scattering measurements, Lebech and Mikke[11] found that the phase transition is still first order in compounds with 0.06% and 0.18% rhenium, but is second order in a sample with 0.7% rhenium. Hence the threshold concentration of impurities probably lies somewhere between 0.1% and 0.2%.

Several ideas have been advanced to explain the profound effect of impurities on the first-order transition. Falicov and Penn[10] speculated that the most important effect of vanadium impurities is to decrease the wave vector Q and increase the incommensurability of the SDW. According to YS, however, the first-order transition is destroyed by impurity scattering, which breaks electron-hole pairs and suppresses both the SDW order parameter g and CDW order parameter $\delta \propto g^2$. Significantly, the theory of YS does not consider the effect of impurities on the wave vector Q or on the other band-structure parameters such as the quasiparticle energies near the Fermi surface. Unfortunately, the numerical estimates of YS were incompatible with a threshold concentration as small as 0.2%.

In this paper we use the formalisms of Zittartz[8] and YS to calculate the threshold concentration of impurities. Our results for the modified SDW and CDW order parameters in the presence of impurities differ somewhat from the results of YS. After including correction terms neglected by YS, we obtain a threshold impurity concentration for vanadium between 0.15% and 0.2%, depending on the cutoff energy ε_0. Therefore a small impurity threshold can be explained solely by impurity scattering, without considering the effects of impurities on the band structure of chromium.

In order to obtain analytic results near the Néel temperature, we expand the mean-field equations in powers of Γ/T_N and T_N/z_0, where Γ is the energy width produced by impurity scattering and z_0 is the energy mismatch between the hole Fermi surfaces. Since[12] $\Gamma \approx 3$ meV, $T_N \approx 27$ meV, and $z_0 \approx 500$ meV, the energy scales are fairly well separated. The final parameter of the theory is the cutoff energy ε_0, which determines the Coulomb interaction λ in terms of T_N. Because this energy is not fixed experimentally, we only assume that ε_0 lies somewhere between 200 and 500 meV.

This paper is divided into five parts. In Sec. II we review the formalism of YS for the SDW and CDW order parameters. In Sec. III we use this formalism to calculate the jump in the SDW order parameter at T_N in the absence of impurities. This relationship allows us to determine the value of the Coulomb interaction λ' between the hole surfaces in terms of the experimentally known discontinuity of the magnetic moment at T_N. In Sec. IV we use the method of Zittartz to study the effects of impurity scattering. In Sec. V we calculate the threshold concentration of impurities as a function of λ'. Using the result of Sec. III, we finally obtain an expression for the threshold impurity concentration as a function of the jump in the CDW order parameter of pure chromium. In Sec. VI we summarize our results and discuss the possibilities for future experimental work. Several integrals are evaluated in Appendix A; in Appendix B we evaluate the sixth-order g^6 term in the free energy of pure chromium; to first order in Γ, the modified order parameters and frequencies are evaluated in Appendix C; and in Appendix D we evaluate the various contributions of order Γ to the self-consistent equation for the SDW order parameter.

II. YOUNG-SOKOLOFF FORMALISM

In this section we review the formalism of YS for the SDW and CDW order parameters of pure chromium. As expected, the phase transition becomes first order in a narrow range of λ' between λ'_F and λ'_c, which will be evaluated shortly. Because the non-nested contributions to the Néel temperature are included, our results differ slightly from the original results of YS.

Since the band structure of chromium contains two hole and one electron bands, the Green's function $\underline{G}(\mathbf{k},i\omega_n)$ is a 6×6 matrix (accounting for the spin) with Matsubara frequencies $\omega_n = 2\pi T(2n+1)$. Following YS, we write the inverse Green's function as

$$\underline{G}^{-1}(\mathbf{k},i\omega_n)=\begin{pmatrix} [i\omega_n-\varepsilon_a(\mathbf{k})]\underline{1} & -\underline{g} & -\underline{g} \\ -\underline{g} & [i\omega_n-\varepsilon_{b-}(\mathbf{k})]\underline{1} & -\delta\underline{1} \\ -\underline{g} & -\delta\underline{1} & [i\omega_n-\varepsilon_{b+}(\mathbf{k})]\underline{1} \end{pmatrix}, \tag{1}$$

where $\varepsilon_a(\mathbf{k})$ is the energy of the electrons (in band a), while

$$\varepsilon_{b\pm}(\mathbf{k})=\varepsilon_b(\mathbf{k}\mp\mathbf{Q}) \tag{2}$$

are the energies of the holes (in bands $b\pm$). This form for the inverse Green's function assumes that $\partial\neq 0$ and $Q\neq 2\pi/a$. When $\partial=0$, a 4×4 matrix should be used to model the one electron band and one hole band. However, our general results for $\partial\neq 0$ smoothly interpolate with previous results for $\partial=0$. Assuming that the SDW is polarized in the $\hat{\mathbf{n}}$ direction, the SDW order parameter is given by

$$\underline{g}=g\hat{\mathbf{n}}\cdot\boldsymbol{\sigma} \ . \tag{3}$$

Of course, the CDW order parameter $\underline{1}\delta$ is diagonal in the spin indices.

The inverse of Eq. (1) is given by

$$\underline{G}(\mathbf{k},i\omega_n)=\frac{1}{\mathcal{D}}\begin{bmatrix} \underline{1}\{[i\omega_n-\varepsilon_{b+}(\mathbf{k})] \times[i\omega_n-\varepsilon_{b-}(\mathbf{k})]-\delta^2\} & \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}g\{[i\omega_n-\varepsilon_{b+}(\mathbf{k})]+\delta\} & \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}g\{[i\omega_n-\varepsilon_{b-}(\mathbf{k})]+\delta\} \\ \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}g\{[i\omega_n-\varepsilon_{b+}(\mathbf{k})]+\delta\} & \underline{1}\{[i\omega_n-\varepsilon_a(\mathbf{k})] \times[i\omega_n-\varepsilon_{b+}(\mathbf{k})]-g^2\} & \underline{1}\{[i\omega_n-\varepsilon_a(\mathbf{k})]\delta+g^2\} \\ \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}g\{[i\omega_n-\varepsilon_{b-}(\mathbf{k})]+\delta\} & \underline{1}\{[i\omega_n-\varepsilon_a(\mathbf{k})]\delta+g^2\} & \underline{1}\{[i\omega_n-\varepsilon_a(\mathbf{k})] \times[i\omega_n-\varepsilon_{b-}(\mathbf{k})]-g^2\} \end{bmatrix} , \tag{4}$$

where

$$\mathcal{D}=[i\omega_n-\varepsilon_a(\mathbf{k})][i\omega_n-\varepsilon_{b+}(\mathbf{k})][i\omega_n-\varepsilon_{b-}(\mathbf{k})]-[i\omega_n-\varepsilon_a(\mathbf{k})]\delta^2-g^2[i\omega_n-\varepsilon_{b-}(\mathbf{k})]-g^2[i\omega_n-\varepsilon_{b+}(\mathbf{k})]-2g^2\delta \tag{5}$$

is the determinant of $\underline{G}^{-1}$.

Because the traces of the $ab\pm$ matrix elements vanish, the self-consistent equations for the SDW and CDW order parameters are[9]

$$\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}g=-\frac{T}{N}\sum_{n,\mathbf{k}}[\nu_{ab+b-a}\underline{G}^{b+a}(\mathbf{k},i\omega_n)+\nu_{aab-b-}\underline{G}^{ab-}(\mathbf{k},i\omega_n)] , \tag{6}$$

$$\underline{1}\delta=\frac{T}{N}\sum_{n,\mathbf{k}}\left[\underline{1}U_{b-b+b-b+}\sum_{\gamma}G_{\gamma\gamma}^{b-b+}(\mathbf{k},i\omega_n)-\nu_{b-b-b+b+}\underline{G}^{b-b+}(\mathbf{k},i\omega_n)\right] , \tag{7}$$

where the direct interaction $U_{\alpha\beta\gamma\delta}$ only couples quasiparticles with the same spin and the exchange interaction $\nu_{\alpha\beta\gamma\delta}$ is spin independent.

It is straightforward to show that $\langle S_{iz}\rangle$ is proportional to the SDW order parameter g and oscillates with wave vector $\mathbf{Q}$. The charge density, on the other hand, is proportional to the CDW order parameter δ and oscillates with wave vector $2\mathbf{Q}$. The formalism of YS ignores higher harmonics of the SDW which may be induced by the coupling between the charge- and spin-density waves.

Substituting the matrix elements of the Green's function into the self-consistent equations, we find

$$g=-\frac{\nu}{N}T\sum_{n,\mathbf{k}}\frac{i\omega_n-\varepsilon_{b-}(\mathbf{k})+\delta}{\mathcal{D}}g , \tag{8}$$

$$\delta=-\frac{\nu'}{N}T\sum_{n,\mathbf{k}}\frac{[i\omega_n-\varepsilon_a(\mathbf{k})]\delta+g^2}{\mathcal{D}} , \tag{9}$$

where

$$\nu=\nu_{aab-b-}+\nu_{ab+b-a} , \tag{10}$$

$$\nu'=\nu_{b-b-b+b+}-2U_{b-b+b-b+} \tag{11}$$

are the modified effective interactions. If $\nu'=0$, but $\nu\neq 0$, then the CDW order parameter vanishes, but the SDW order parameter is nonzero. On the other hand, if $\nu=0$, then both g and δ vanish except for the particular value of ν' satisfying Eq. (9) with $g=0$. For any other value of ν', both ν and ν' must be nonzero to support a CDW.

If ν' and δ vanish, then Eq. (8) for g is formally identical to the self-consistent equation for the superconducting order parameter Δ in BCS theory. Like Δ, g also has the significance of an energy gap. The interacting quasiparticle energies are found by setting $\mathcal{D}=0$. If $\delta=0$, the Coulomb interaction ν produces an energy gap of $2g$ at the Fermi surface. As in BCS theory, the zero-temperature value of g is then given by $g(0)=1.76T_N$. If ν' and δ are nonzero, however, the straightforward analogy with BCS theory disappears and the set of self-consistent equations becomes more complicated.

The integrals over momentum can be evaluated by using the simple form for the electron and hole energies originally proposed by Falicov and Penn:[10]

$$\varepsilon_a(\mathbf{k})=z , \tag{12a}$$

$$\varepsilon_{b+}(\mathbf{k})=-z , \tag{12b}$$

$$\varepsilon_{b-}(\mathbf{k})=-z+z_0 , \tag{12c}$$

where $z=v_Fk-\varepsilon_F$ is the energy of an electron measured from the Fermi energy and $z_0\approx 500$ meV is the energy mismatch[12] between the two hole surfaces. Relations (12a)–(12c) are valid over the portion of the Fermi surface shown in Fig. 1(b), which is nested by the $b+$ and a bands. Because of the symmetry between the two halves of the Fermi surface, all integrals can be evaluated with these energies. As $|\partial|$ decreases, Q approaches $2\pi/a$ and z_0 tends to zero. In that limit, of course, only two bands survive and $\varepsilon_{b+}(\mathbf{k})=\varepsilon_{b-}(\mathbf{k})$.

Since δ is of order g^2, it does not contribute to the linearized self-consistent equation for g:

$$1=-\lambda\int_{-\varepsilon_0}^{\varepsilon_0}\frac{dz}{z}f(z)-\lambda\int_{-\varepsilon_0}^{\varepsilon_0}\left[\frac{f(z)}{2z-z_0}+\frac{f(z_0-z)}{z_0-2z}\right], \tag{13}$$

where $f(z)=1/[\exp(\beta z)+1]$ is the Fermi function. The coupling constant $\lambda=\nu\rho(\varepsilon_F)/2$ is proportional to half the density of states at the Fermi surface. The first term in Eq. (13) is produced by the nested portion of the Fermi surface; the second term, which was neglected by YS, is produced by the pairing between non-nested electrons and holes with energies differing by z_0.

As usual, the cutoff ε_0 is required to obtain convergent integrals and signifies the energy below which the quasiparticle excitations are well defined. Physically, the cutoff must be much larger than the zero-temperature order parameter $g(0)\approx 0.06$ eV and much smaller than the Fermi energy[13] $\varepsilon_F\approx 1$ eV. Since z_0 provides a natural energy scale for the problem, we believe that ε_0 lies slightly below z_0. However, all of our results will be plotted as functions of the cutoff between 200 and 500 meV.

Evaluating the first integral in Eq. (13), we obtain the Néel temperature of pure chromium:

$$T_{N0}=1.13\varepsilon_0 e^{(2G-1/\lambda)}, \tag{14}$$

where

$$G=-\frac{1}{2}\int_{-\varepsilon_0}^{\varepsilon_0}dz\left[\frac{f(z)}{2z-z_0}+\frac{f(z_0-z)}{z_0-2z}\right] \tag{15}$$

is evaluated at T_{N0}. Because G is logarithmically divergent, the integral over energy must be cut off at ε_0. When $z_0=0$, $G(T_{N0})=1/(4\lambda)$ and we recover the result of Zittartz[8] for T_{N0} when chromium has only two bands. When $z_0\approx\varepsilon_0$, $G(T_{N0})\approx 0.3$, and the non-nested portion of the Fermi surface multiplies the result of YS by about 1.8. Hence the non-nested contribution to Eq. (14) lowers the value of λ required to produce a given Néel temperature.

In Fig. 2 we plot λ versus the cutoff ε_0 using $T_{N0}=26.7$ meV and $z_0=500$ meV. As expected, the coupling constant λ is a decreasing function of ε_0. For values of ε_0 between 400 and 500 meV, λ lies between 0.30 and 0.27. If the non-nested portion of the Fermi surface was neglected, λ would increase by about 25%.

Using the quasiparticle energies of Eq. (12), we can also evaluate δ to order g^2:

$$\delta=-2\frac{\nu'}{z_0\nu}\frac{g^2}{D}(1-4\lambda G), \tag{16}$$

where D is given by

$$D=1+\frac{\nu'}{N}\sum_{\mathbf{k}}\frac{f(\varepsilon_{b+})-f(\varepsilon_{b-})}{\varepsilon_{b+}-\varepsilon_{b-}}. \tag{17}$$

Expanding the difference of Fermi functions in powers of z_0, we find that[14]

$$D=1-2\lambda', \tag{18}$$

where $\lambda'=\nu'\rho(\varepsilon_F)/2$ is the coupling constant between holes. When $\lambda'=\lambda'_c\equiv\frac{1}{2}$, the self-consistent equation for δ has a nontrivial solution even when $g=0$. So, at λ'_c, a CDW can exist without a SDW. For all other values of λ', both above and below λ'_c, δ is proportional to g^2 and a CDW cannot exist in the absence of a SDW.

Because G approaches $1/(4\lambda)$ very rapidly as $z_0\rightarrow 0$, δ vanishes as the SDW becomes commensurate. But, for large z_0, δ falls off like $1/z_0$. Numerically, δ/g^2 reaches a maximum when $z_0\approx 0.95\varepsilon_0$.

To evaluate the self-consistent equation for g to order g^3 is rather complicated. Because z_0 is large compared with T_{N0}, this task can be simplified by neglecting the non-nested contributions to the self-consistent equation. With the two exceptions mentioned below, terms of order T_{N0}/z_0 and higher can be safely neglected in Eq. (8). The first exception is that the logarithmically divergent integral G is always retained, even though it is formally of order $(\varepsilon_0/z_0)^2$. The second exception is introduced because the CDW order parameter δ diverges as λ' approaches λ'_c. Since λ' is very close to $\lambda'_c=\frac{1}{2}$, $1-2\lambda'$ is taken to be of order $(T_{N0}/z_0)^2$. Therefore δ is of order z_0 and terms of order $(T_{N0}/z_0)^2/(1-2\lambda')$ are retained in the self-consistent equation for g.

Expanding Eq. (8) to order g^3 and neglecting terms of order $(T_{N0}/z_0)^2$, we find that

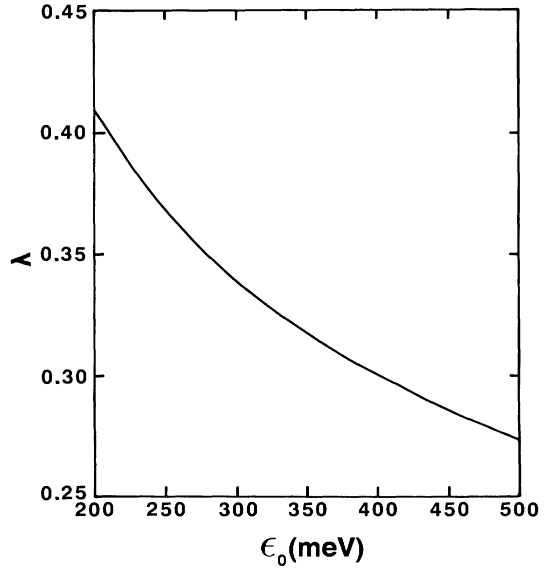

FIG. 2. Coupling constant λ vs the energy cutoff ε_0 for $T_{N0}=26.7$ meV and $z_0=500$ meV.

$$g^2\left[\frac{7}{8\pi^2}\frac{\zeta(3)}{T^2}-\frac{4\lambda'}{\lambda^2 z_0^2}\frac{(1-4\lambda G)^2}{1-2\lambda'}\right]=-\ln\left[\frac{T}{T_{N0}}\right], \tag{19}$$

where $\zeta(3)\approx 1.204$ is the Riemann ζ function defined in Appendix A. The various integrals in the self-consistent equation have been evaluated in Appendix A and B. When G is neglected, this expression agrees with the result of YS. If $\lambda'=0$, the expression in brackets is positive and Eq. (19) has no solution for g when $T>T_{N0}$. The transition is then second order. But if the second term in brackets exceeds the first, then a nontrivial solution for g exists when $T>T_{N0}$. In that case the transition is first order. These two regimes are shown schematically in Fig. 3(a), where the order parameter is plotted versus temperature.

To obtain the threshold value of λ', above which the transition becomes first order, we set the expression in brackets to zero. This yields

$$\frac{\lambda'_F}{1-2\lambda'_F}=\frac{7}{32\pi^2}\frac{\lambda^2\zeta(3)}{(1-4\lambda G)^2}\left[\frac{z_0}{T_{N0}}\right]^2 \tag{20}$$

or, with the dimensionless parameter $\gamma=z_0/2\pi T_{N0}$,

$$\lambda'_F=\frac{1}{2}\left[1+(1-4\lambda G)^2\frac{4}{7\lambda^2\gamma^2\zeta(3)}\right]^{-1}, \tag{21}$$

which is plotted in the lower curve of Fig. 4. When ε_0 equals z_0, G is approximately 0.30 and λ'_F is close to 0.39. Note that λ'_F initially decreases as ε_0 increases, but passes through a minimum slightly above z_0.

So the phase transition of chromium is first order if the Coulomb interaction λ' lies in a narrow window of values between $\lambda'_F\approx 0.4$ and $\lambda'_c=0.5$. If λ' exceeds λ'_c, then the expression in brackets is again positive and the transition is second order. In the limit $z_0\to 0$, $G\to 1/(4\lambda)$, so that both the numerator and denominator of Eq. (20) vanish. However, Eq. (20) was derived by assuming that $z_0 \gg T_{N0}$. If the threshold was evaluated exactly, then the numerator in Eq. (20) would vanish more slowly than the denominator. So, as $z_0\to 0$, $\lambda'_F\to\frac{1}{2}$ and the window of values between λ'_F and $\frac{1}{2}$ shrinks to zero. In order to obtain a first-order transition with a small value of z_0, chromium must be on the brink of a CDW instability.

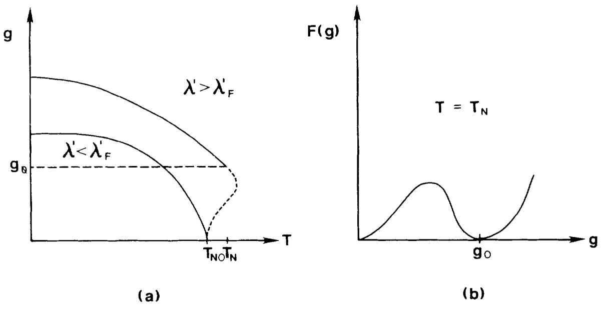

FIG. 3. Schematic drawing of the SDW order parameter g vs T for the second-order regime ($\lambda'<\lambda'_F$) and the first-order regime ($\lambda'>\lambda'_F$). Also shown is the free energy vs g at the Néel temperature T_N in the first-order regime.

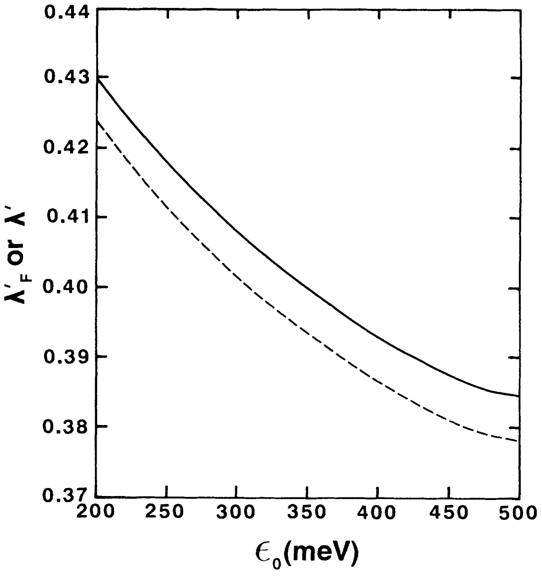

FIG. 4. Threshold value λ'_F (dashed) above which the transition becomes first-order and the true value of λ' (solid) vs the cutoff ε_0. This figure uses the same parameters as Fig. 2 as well as $g_0/T_{N0}=0.71$.

Generally, the phase transition is weakly first order when λ' just exceeds λ'_F. The transition becomes more strongly first order as λ' approaches the CDW instability at λ'_c. As shown in Fig. 3(b), the true Néel temperature in the first-order regime is no longer given by T_{N0}. In order to evaluate T_N, we must expand the self-consistent equation to order g^5. This task will be undertaken in the next section.

III. FIRST-ORDER TRANSITION IN PURE CHROMIUM

In this section we calculate the true Néel temperature T_N and the jump g_0 in the order parameter at T_N in the first-order regime $\lambda'_F<\lambda'<\lambda'_c$. To do so we construct an effective free energy $F(g)$, which can be expanded near the Néel temperature in powers of g^2:

$$F(g)=A_1g^2+A_2^2g^4+A_3g^6+\cdots, \tag{22}$$

where we set $F(0)=0$. Using this free energy, we can obtain analytic results for g_0 and T_N. In the original work of YS, g_0 and T_N were evaluated numerically.

The self-consistent equation for g is given by the condition $dF/dg=0$. Retaining only the three lowest-order terms in Eq. (22), we find

$$A_1+2A_2g^2+3A_3g^4=0\ . \tag{23}$$

In the first-order regime, the Néel temperature T_N and jump g_0 of the order parameter at T_N are obtained by setting $F(g)=0$, as shown in Fig. 3(b). This condition can be written

$$A_1+A_2g^2+A_3g^4=0\ . \tag{24}$$

Together with Eq. (23), this relation fixes g_0 at

$$g_0^2=-\frac{A_2}{2A_3}\ . \tag{25}$$

When the transition becomes first order, A_1 changes sign from negative to positive and A_2 changes sign from positive to negative. From Eq. (25) we conclude that A_3 must be positive in the first-order regime. The Néel temperature is now obtained by substituting Eq. (25) into either Eq. (23) or (24), with the result

$$4A_1A_3=A_2^2\ . \tag{26}$$

As $g_0\rightarrow 0$, both A_1 and A_2 tend to zero and T_N approaches T_{N0}, which is given by the condition $A_1=0$.

The coefficients A_1, A_2, and A_3 can be determined up to a constant by writing the self-consistent equation for g in the form of Eq. (24). Therefore, Eq. (19) implies that

$$A_1=\frac{\lambda}{2}\ln\left[\frac{T}{T_{N0}}\right]\ , \tag{27}$$

$$A_2=-\frac{\lambda'}{\lambda z_0^2}\,\frac{(1-4\lambda G)^2}{1-2\lambda'}+\frac{7\lambda}{32\pi^2}\,\frac{\zeta(3)}{T^2}\ , \tag{28}$$

where the sign of A_1 is chosen to be positive for $T>T_{N0}$. In order to evaluate T_N and g_0, we also need the sixth-order term in the free energy or the fifth-order term in Eq. (8).

To evaluate the fifth-order term in the self-consistent equation for g, we must first calculate the fourth-order term in the self-consistent equation for δ. The result for δ is provided in Appendix B. After expanding the self-consistent equation for g in terms of δ, we obtain the expression for A_3 in Eq. (B3).

Since T_N is very close to T_{N0} and λ' is very close to λ'_F, A_3 may be evaluated at T_{N0} and λ'_F:

$$A_3\big|_{\lambda'_F,T_{N0}}=\frac{49\zeta(3)^2}{128\pi^4T_{N0}^4}\,\frac{\lambda^2}{1-4\lambda G}-\frac{31\lambda\zeta(5)}{256\pi^4T_{N0}^4}\ . \tag{29}$$

Also, since A_2 is very small near the threshold for the first-order transition, this coefficient may be linearized in powers of $(\lambda'-\lambda'_F)$:

$$A_2\approx-\frac{\lambda'-\lambda'_F}{\lambda}\left[\frac{7\lambda^2}{16\pi^2}\zeta(3)\right]^2\left[\frac{z_0}{T_{N0}}\right]^2\frac{1}{(1-4\lambda G)^2}\ , \tag{30}$$

which anticipates the fact that T_N-T_{N0} is of order $(\lambda'-\lambda'_F)^2$.

Using Eq. (26), we find that the first-order Néel temperature is given by

$$\frac{T_N-T_{N0}}{T_{N0}}=\frac{1}{2}\left[\frac{7\lambda\zeta(3)}{4\pi}\right]^4\left[\frac{z_0}{T_{N0}}\right]^2\frac{(\lambda'-\lambda'_F)^2}{(1-4\lambda G)^3}\times[98\lambda\zeta(3)^2-31\zeta(5)(1-4\lambda G)]^{-1}\ . \tag{31}$$

Note that T_N-T_{N0} is proportional to $(\lambda'-\lambda'_F)^2$ and grows as $\lambda'-\lambda'_F$ increases or as the transition becomes more strongly first order. Also, as expected, the first-order Néel temperature T_N is slightly larger than the second-order transition temperature T_{N0}. Since we have linearized A_2 in $\lambda'-\lambda'_F$, Eq. (31) assumes that λ' is smaller than the critical value $\lambda'_c=\frac{1}{2}$, above which the transition is once again second order.

Using Eq. (25), we finally find that the jump of the order parameter at T_N is given by

$$\left[\frac{g_0}{T_{N0}}\right]^2=\left[\frac{z_0}{T_{N0}}\right]^2\frac{49\zeta(3)^2\lambda^2(\lambda'-\lambda'_F)}{2(1-4\lambda G)}\times[98\lambda\zeta(3)^2-31\zeta(5)(1-4\lambda G)]^{-1}\ . \tag{32}$$

Because g_0/T_{N0} scales like $(\lambda'-\lambda'_F)^{1/2}$, the first-order transition becomes weaker as λ' approaches the threshold λ'_F from above. Of course, Eqs. (31) and (32) assume that λ' is above the threshold λ'_F so that g_0 is real.

While the jump in the order parameter cannot be measured directly, the jump in the rms magnetic moment at T_N can be measured by neutron scattering[12] and is given by $\mu(T_N^-)/\mu(0)=0.27$, where $\mu(0)$ is the rms magnetic moment at $T=0$. Because the SDW order parameter g is proportional to the magnetic moment, the ratio $g_0/g(0)$ also equals 0.27. As discussed earlier, the order parameter is itself proportional to the energy gap at the Fermi surface. If $\delta=0$, then the energy gap at the Fermi surface is $2g$. Using the experimental value[12] of 0.12 eV for the energy gap at low temperatures, we estimate that $g(0)\approx 0.062$ eV. Alternatively, the zero-temperature gap can be estimated from the BCS-like relation $g(0)=1.76T_N\approx 0.047$ eV, which also assumes that $\delta=0$. If δ is nonzero, then YS find that $g_0\approx 0.055$ eV. Because $g(0)$ may be somewhat larger[9] than this, we use 0.07 eV as a conservative estimate for $g(0)$. The ratio g_0/T_{N0} is then approximately 0.71.

Using this value for g_0/T_{N0}, we plot λ' versus the cutoff ε_0 in the upper curve of Fig. 4. Like λ'_F, λ' also passes through a minimum slightly above z_0. Because the phase transition is weakly first order, the coupling constant λ' is close to the threshold value λ'_F, differing by about 0.007.

IV. IMPURITIES

In order to study the effects of impurity scattering, we must generalize the formalism of Zittartz,[8] which was originally designed for a metal with only two bands. Fortunately, only minor changes are required to accommodate the presence of two hole surfaces instead of one. Because it breaks electron-hole pairs, impurity scattering suppresses the SDW order parameter g and the Néel temperature T_{N0}.

Following Zittartz, we replace the order parameters g and δ in the inverse Green's function $\underline{G}^{-1}$ by the modified, frequency-dependent quantities $\tilde{g}_n$ and $\tilde{\delta}_n$:

$$\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\tilde{g}_n=\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}g+\frac{\Gamma}{2\pi mk_F}\int_0^\infty dp\,p^2\underline{G}_{ab-}(p,i\omega_n)\ , \tag{33}$$

$$\underline{1}\tilde{\delta}_n = \underline{1}\delta + \frac{\Gamma}{2\pi m k_F}\int_0^\infty dp\, p^2 \underline{G}_{b-b+}(p, i\omega_n) , \tag{34}$$

where

$$\Gamma = \frac{\rho_{\mathrm{sc}} k_F m}{4\pi^2}\int d\Omega |u(\theta)|^2 \tag{35}$$

is the energy width produced by impurity scattering and $1/\Gamma$ is the scattering lifetime of electrons and holes near the Fermi surface. In Eqs. (33)–(35), m is the mass of a quasiparticle, k_F is the Fermi wave vector, ρ_{sc} is the density of impurities, and $u(\theta)$ is the impurity potential.

An angular average has already been performed over the Green's-function matrix elements in Eqs. (33) and (34). Therefore the remaining momentum integral over p implicity averages the nested and non-nested portions of the Fermi surface.

The Matsubara frequencies ω_n in $\underline{G}^{-1}$ must also be replaced by the modified frequencies $\tilde{\omega}_n^{a,b}$, where

$$\underline{1} i\tilde{\omega}_n^{a,b} = \underline{1} i\omega_n - \frac{\Gamma}{2\pi m k_F}\int_0^\infty dp\, p^2 \underline{G}_{aa,b\pm b\pm}(p, i\omega_n) . \tag{36}$$

Although the electron and hole frequencies are now different, the symmetry between the $b\pm$ bands guarantees that $\tilde{\omega}_n^{b+} = \tilde{\omega}_n^{b-}$.

The modified self-consistent equations are now given by

$$g = -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k}) + \tilde{\delta}_n}{\mathcal{D}'} \tilde{g}_n , \tag{37}$$

$$\delta = -\frac{\nu'}{N} T \sum_{n,\mathbf{k}} \frac{[i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})]\tilde{\delta}_n + \tilde{g}_n^2}{\mathcal{D}'} , \tag{38}$$

where

$$\begin{aligned}\mathcal{D}' = {} & [i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})][i\tilde{\omega}_n^b - \varepsilon_{b+}(\mathbf{k})][i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k})] \\ & - [i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})]\tilde{\delta}_n^2 - \tilde{g}_n^2[i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k})] \\ & - \tilde{g}_n^2[i\tilde{\omega}_n^b - \varepsilon_{b+}(\mathbf{k})] - 2\tilde{g}_n^2\tilde{\delta}_n \end{aligned} \tag{39}$$

is the modified determinant.

The Green's function of Eq. (4) is now replaced by

$$\underline{G}(\mathbf{k}, i\omega_n) = \frac{1}{\mathcal{D}'}\begin{bmatrix} \begin{matrix}\underline{1}\{[i\tilde{\omega}_n^b - \varepsilon_{b+}(\mathbf{k})] \\ \times[i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k})] - \tilde{\delta}_n^2\}\end{matrix} & \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\tilde{g}_n\{[i\tilde{\omega}_n^b - \varepsilon_{b+}(\mathbf{k})] + \tilde{\delta}_n\} & \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\tilde{g}_n\{[i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k})] + \tilde{\delta}_n\} \\ \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\tilde{g}_n\{[i\tilde{\omega}_n^b - \varepsilon_{b+}(\mathbf{k})] + \tilde{\delta}_n\} & \begin{matrix}\underline{1}\{[i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})] \\ \times[i\tilde{\omega}_n^b - \varepsilon_{b+}(\mathbf{k})] - \tilde{g}_n^2\}\end{matrix} & \underline{1}\{[i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})]\tilde{\delta}_n + \tilde{g}_n^2\} \\ \hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\tilde{g}_n\{[i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k})] + \tilde{\delta}_n\} & \underline{1}\{[i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})]\tilde{\delta}_n + \tilde{g}_n^2\} & \begin{matrix}\underline{1}\{[i\tilde{\omega}_n^a - \varepsilon_a(\mathbf{k})] \\ \times[i\tilde{\omega}_n^b - \varepsilon_{b-}(\mathbf{k})] - \tilde{g}_n^2\}\end{matrix} \end{bmatrix} . \tag{40}$$

Since $\tilde{g}_n$, $\tilde{\delta}_n$, $\tilde{\omega}_n^a$, and $\tilde{\omega}_n^a$ are themselves evaluated in terms of the matrix elements of this Green's function, Eqs. (33)–(40) must be solved consistently.

Because we are interested in very small concentrations of impurity, the self-consistent equations may be linearized in Γ. Therefore Eqs. (33), (34), and (36) can be evaluated by setting $\Gamma = 0$ in each of the integrands. As usual, the momentum integrals are evaluated by using the electron and hole energies of Eq. (12). Since the Fermi energy $\varepsilon_F \approx 1$ eV is much larger than the temperature or z_0, we replace the lower limits of integration by $-\infty$. The results for $\tilde{\delta}_n$, $\tilde{g}_n$, and the Matsubara frequencies $\tilde{\omega}_n^a$ and $\tilde{\omega}_n^b$ are contained in Appendix C. To zero order in g, both Matsubara frequencies equal $\tilde{\omega}_n$ given by Eq. (C3). But to order g^2, $\tilde{\omega}_n^a$ and $\tilde{\omega}_n^b$ differ by a term of order $\Gamma g^2/T$.

The second-order Néel temperature $\tilde{T}_{N0}$ in the presence of impurities is now evaluated with the modified self-consistent equation to zeroth order in g:

$$1 = -\frac{\nu}{N}\sum_{n,\mathbf{k}} \frac{\tilde{g}_n}{g} \frac{1}{i\tilde{\omega}_n - \varepsilon_a} \frac{1}{i\tilde{\omega}_n - \varepsilon_{b+}} . \tag{41}$$

Expanding this relation to first order in Γ, we find that

$$\begin{aligned}\ln\left[\frac{T}{T_{N0}}\right] = {} & -\frac{3\pi}{16}\frac{\Gamma}{T} - \frac{5\pi}{2}\Gamma T \sum_{n=0}^{\infty} \frac{1}{\omega_n^2 + z_0^2/4} \\ & + \frac{3\pi}{4}\Gamma T z_0^2 \sum_{n=0}^{\infty} \frac{1}{(\omega_n^2 + z_0^2/4)^2} \\ & + 2[G(T) - G(T_{N0})] . \end{aligned} \tag{42}$$

Because the non-nested contribution to $\tilde{g}_n$ was retained, this expression is exact to first order in Γ. If $z_0 = 0$, then the difference

$$G(T) - G(T_{N0}) = -\frac{1}{2}\ln\left[\frac{T}{T_{N0}}\right] \tag{43}$$

is of order Γ/T and the modified Néel temperature

$$\tilde{T}_{N0} = T_{N0} - \frac{\pi\Gamma}{4} \tag{44}$$

agrees with the result of Zittartz[8] when the electron and hole bands are perfectly nested.

More generally, the difference between the G functions can be written

$$G(T) - G(T_{N0}) = (T - T_{N0})\left.\frac{dG}{dT}\right|_{T_{N0}} . \tag{45}$$

For large z_0, $G(T)$ is of order $(\varepsilon_0/z_0)^2$ and dG/dT is of order $1/z_0$. In that case Eq. (45) is of order Γ/z_0 and the last term in Eq. (42) can be neglected. In this limit the second and third terms on the right-hand side of Eq. (42) can also be neglected. Therefore the modified second-order Néel temperature in chromium is given by

$$\tilde{T}_{N0}=T_{N0}-\frac{3\pi}{16}\Gamma \ . \tag{46}$$

Because the non-nested portion of the Fermi surface does not effectively contribute to the impurity scattering, this result is *larger* than the result of Zittartz with $z_0=0$ (assuming that T_{N0} is fixed).

Because Γ is always positive, Eq. (46) implies that impurity scattering always suppresses the Néel temperature. While the Néel temperature is suppressed with vanadium doping, the Néel temperature is actually enhanced by doping with manganese.[6] Since it has more conduction electrons than chromium, manganese decreases z_0 and increases the commensurability of the SDW. Experimentally,[6] doping with manganese increases the Néel temperature until the SDW becomes commensurate with the lattice when $T_N \approx 700$ K.

But, so far, we have neglected the effects of impurities on the band structure of chromium. The wave vector Q, the mismatch energy z_0, and the quasiparticle energies $\varepsilon_{b\pm}(\mathbf{k})=\varepsilon_b(\mathbf{k}\mp\mathbf{Q})$ are all affected by doping with impurities. In addition, the density of states $\rho(\varepsilon_F)$ and the coupling parameters λ and λ', which are proportional to $\rho(\varepsilon_F)$, may also be affected by the presence of impurities.

While impurity scattering may be the most important effect of doping with vanadium, the dominant effects of doping with manganese are the increased commensurability of the SDW and the enhanced electron-hole pairing between the non-nested Fermi surfaces. As discussed in Sec. II, the function G of Eq. (15) measures the coupling between electrons and holes on the non-nested Fermi surfaces. When z_0 decreases, both G and the Néel temperature T_{N0} of Eq. (14) increase. The dependence of T_{N0} on z_0 is shown in Fig. 5, where we fix $\varepsilon_0=500$ meV and $\lambda=0.273$, so that $T_{N0}=310$ K when $z_0=500$ meV. The increase of T_{N0} with decreasing z_0 is very rapid because $G(z_0)$ is a very sensitive function of its argument when $z_0<0.8\varepsilon_0$.

In order to calculate the correction to Eq. (46) for small concentrations of impurities, we expand T_{N0} to first order in Γ as

$$T_{N0}(\Gamma)=T_{N0}(0)+\alpha\Gamma \ , \tag{47}$$

$$\alpha=\frac{dT_{N0}}{dz_0}\,\frac{dz_0}{d\Gamma}\bigg|_{\Gamma=0}=2T_{N0}\frac{dG}{dz_0}\,\frac{dz_0}{d\Gamma}\bigg|_{\Gamma=0} \ . \tag{48}$$

The dimensionless parameter α is negative for vanadium doping but positive for manganese doping. Together with Eq. (46), this relation implies that the second-order Néel temperature is given by

$$\tilde{T}_{N0}=T_{N0}(0)+\left\{\alpha-\frac{3\pi}{16}\right\}\Gamma \ . \tag{49}$$

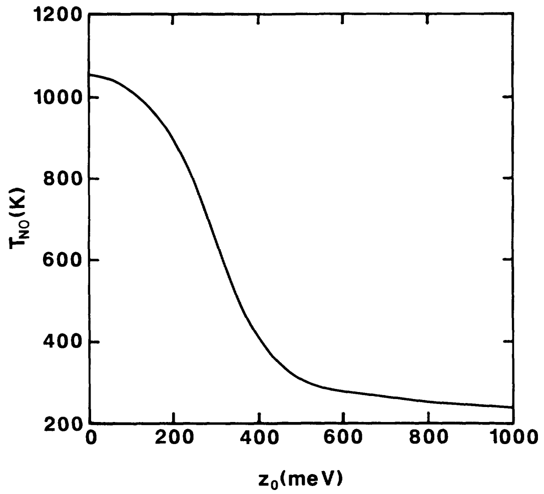

FIG. 5. Néel temperature T_{N0} vs z_0 with $\varepsilon_0=500$ meV and $\lambda=0.273$.

If α is smaller than $3\pi/16$, then small concentrations of impurities will suppress the Néel temperature. But if α is larger than $3\pi/16$, then the Néel temperature will be enhanced by impurities.

For large z_0, $z_0\,dG/dz_0$ is independent of temperature and scales like $(\varepsilon_0/z_0)^2$. If the wave vector Q is a linearly increasing (or decreasing) function of vanadium (or manganese) concentration,[6] then $dz_0/d\Gamma$ scales like z_0/T_{N0} and the band-structure parameter α scales like $(\varepsilon_0/z_0)^2$. Therefore α may not be negligible compared to $3\pi/16$.

Because the Néel temperature increases with manganese doping, α must exceed $3\pi/16$ in Cr-Mn alloys. Although Fig. 5 yields a commensurate Néel temperature T_{N0} of about 1050 K, the measured Néel temperature of 700 K in $\mathrm{Cr_{0.94}Mn_{0.06}}$ also includes the effects of impurity scattering and of electron-phonon scattering, which becomes increasingly important as the Néel temperature grows. In vanadium alloys α is negative and the Néel temperature decreases with doping. Significantly, the Néel temperature also decreases when chromium is alloyed with isoelectric elements like molybdenum or tungsten.[6] In such compounds the band-structure parameter α can be neglected and impurity scattering dominates.

Since the band-structure parameter α can have a significant effect on the Néel temperature, we will retain this parameter in the next section. However, as mentioned above, impurities can also affect other band-structure parameters such as the coupling constants λ and λ'. In order to keep the formalism fairly simple, we neglect these other changes in band structure with doping.

Generally, Γ can be estimated from the residual resistivity at zero temperature. However, such an estimate would require knowledge of the electron effective mass. Alternatively, we may use Eq. (46) with $\alpha=0$ and the measured Néel temperatures to obtain an upper or lower bound on Γ. In Cr-V alloys, α is negative and this estimate would provide an upper bound on Γ. Noakes, Holden, and Fawcett[2] found that doping with 0.2% vanadium lowers the Néel temperature from 310 to 289 K. Since $T_N \approx T_{N0}$, Eq. (46) implies that $\Gamma/T_{N0} \approx 0.115$. For small amounts of vanadium, Γ is a linear function of the impurity concentration and $\Gamma \approx (178\ \mathrm{K}) \times c_v$, where c_v is the percentage of vanadium.

V. THRESHOLD IMPURITY CONCENTRATION

In this section we calculate the threshold value of Γ, above which the transition becomes second order. First, we obtain an expression for Γ_F/T_{N0} as a function of $\lambda' - \lambda'_F$. Then we use the results of Sec. III to express this threshold in terms of the jump g_0 of the order parameter in pure chromium at its first-order Néel temperature. Our final results do not depend on the band-structure parameter α.

To solve for the CDW order parameter δ in terms of the SDW order parameter g, we expand Eq. (38) to second order in g and first order in Γ. While the denominator D of δ is unchanged by impurities, the numerator contains two extra contributions:

$$\begin{aligned}\delta &= -\frac{\nu'}{N}\frac{1}{1-2\lambda'}T \\ &\quad \times \sum_{n,\mathbf{k}} \tilde{g}_n^2 \frac{1}{(i\tilde{\omega}_n - \varepsilon_a)(i\tilde{\omega}_n - \varepsilon_{b+})(i\tilde{\omega}_n - \varepsilon_{b-})} \\ &= -2\frac{\lambda'}{1-2\lambda'} \\ &\quad \times \frac{g^2}{\lambda z_0}\left[1 - 4\lambda G - \frac{\pi}{16}\lambda\frac{\Gamma}{T_{N0}} - \alpha\lambda\frac{\Gamma}{T_{N0}}\right], \qquad (50)\end{aligned}$$

which uses Eq. (49) for $\tilde{T}_{N0} - T_{N0}(0)$. Since dG/dT is of order $1/z_0$ for large z_0, we ignore the Γ dependence of $G(\tilde{T}_{N0})$ and evaluate this function at $T_{N0}(0)$.

As expected, Eq. (50) with $\alpha = 0$ implies that *impurity scattering suppresses the CDW order parameter* δ. However, the effects on δ of changes in band structure are somewhat more complicated. While the effect of impurities on T_{N0} is explicitly included in Eq. (50), we have neglected the direct effect of impurities on the energy mismatch z_0 and on the coupling constants λ and λ'. The actual effect of band-structure changes on the CDW depends on the summations of these many effects. Of course, the net effect of vanadium or manganese impurities on the CDW then depends on the balance between the scattering and band-structure terms.

Although we cannot predict the effect on δ of small concentrations of impurities, we can conclude from Eq. (50) that δ vanishes in the limit $z_0 \to 0$. Because $\tilde{\omega}_n$ is an odd function of ω_n, the summation over Matsubara frequencies vanishes if $z_0 = 0$. So the CDW must vanish when the manganese concentration is sufficiently large that the SDW is commensurate. Further experiments are required to determine the behavior of the CDW for small concentrations of manganese.

While the impurity corrections to δ are of order $\Gamma z_0 g^2/T_{N0}^3$, the correction to $\bar{\delta}_n$ in Eq. (C1) is of order $\Gamma g^2/z_0 T_{N0}$. So, to lowest order in $1/z_0$, $\bar{\delta}_n = \delta$ is given by Eq. (50).

To order g^3 the modified self-consistent equation for g can now be written as

$$\begin{aligned}1 = -\frac{\nu}{N}T\sum_{n,\mathbf{k}}\frac{\tilde{g}_n}{g}\Bigg[&\frac{\tilde{\delta}_n}{(i\tilde{\omega}_n - \varepsilon_a)(i\tilde{\omega}_n - \varepsilon_{b+})(i\tilde{\omega}_n - \varepsilon_{b-})} \\ &+ \frac{1}{(i\tilde{\omega}_n^a - \varepsilon_a)(i\tilde{\omega}_n^b - \varepsilon_{b+})} \\ &+ \frac{\tilde{g}_n^2}{(i\tilde{\omega}_n - \varepsilon_a)^2(i\tilde{\omega}_n - \varepsilon_{b+})^2}\Bigg], \qquad (51)\end{aligned}$$

where we have ignored the non-nested contributions of order $1/z_0$ and higher. Because the second term on the right-hand side is of order 1, we preserve the g dependence of the frequencies $\tilde{\omega}_n^a$ and $\tilde{\omega}_n^b$ in this term. In all the other terms, which are of order g^2, the frequencies are evaluated to zeroth order in g.

The various contributions to Eq. (51) are evaluated to order Γ in Appendix D. After a lengthy calculation, we find that

$$\begin{aligned}g^2\left[1 - \frac{3\pi}{16}\frac{\Gamma}{T_{N0}}\right]\Bigg[&\frac{7\zeta(3)}{8\pi^2}\frac{1}{T_{N0}^2} - \frac{7\zeta(3)}{4\pi^2}\frac{\Gamma}{T_{N0}^3}\left[\alpha - \frac{3\pi}{16}\right] \\ &- \frac{23\pi}{768}\frac{\Gamma}{T_{N0}^3} - \frac{4}{\lambda^2 z_0^2}\frac{\lambda'}{1-2\lambda'}(1-4\lambda G)\left[1 - 4\lambda G - \frac{\pi}{8}\lambda\frac{\Gamma}{T_{N0}} - 2\alpha\lambda\frac{\Gamma}{T_{N0}}\right]\Bigg] = -\ln\left[\frac{T}{T_{N0}}\right], \qquad (52)\end{aligned}$$

where T_{N0} is evaluated with $\Gamma = 0$ and G is evaluated at T_{N0}. Because the correction terms of order Γ with $\alpha = 0$ are positive, *impurity scattering suppresses the SDW order parameter g*. As for the CDW order parameter, the changes in band structure with doping can either enhance or suppress the SDW order parameter.

Of course, the threshold value for Γ is obtained by setting the expression in brackets equal to zero. After linearizing in $\lambda' - \lambda'_F$, we find that

$$\begin{aligned}\frac{\Gamma_F}{T_{N0}} &= 12\pi\left[\frac{7\lambda\zeta(3)}{\pi^2}\right]^2\left[\frac{z_0}{T_{N0}}\right]^2\frac{\lambda' - \lambda'_F}{1-4\lambda G} \\ &\quad \times \{84\zeta(3)[3(1+4\lambda G)+\lambda] - 23\pi^2(1-4\lambda G)\}^{-1}, \qquad (53)\end{aligned}$$

where the corrections involving the band-structure parameter α have canceled. As expected, the threshold value decreases as $\lambda' - \lambda'_F$ decreases.

Finally, we can use Eq. (32) for the jump g_0 in the SDW order parameter when $\Gamma = 0$ to write

$$\frac{\Gamma_F}{T_{N0}} = \left[\frac{g_0}{T_{N0}}\right]^2 \frac{24}{\pi^3}[98\lambda\zeta(3)^2 - 31\zeta(5)(1-4\lambda G)] \times \{84\zeta(3)[3(1-4\lambda G)+\lambda] - 23\pi^2(1-4\lambda G)\}^{-1} . \tag{54}$$

This relation, which is the most important result of our work, determines the threshold concentration of impurities in terms of the experimentally determined jump in the SDW order parameter in the absence of impurities. The only quantity which cannot be fixed by experiment is the energy cutoff ε_0, which affects the values of λ and G.

With $g_0/T_{N0} = 0.71$, the threshold Γ_F/T_{N0} is plotted versus ε_0 in Fig. 6. Like λ'_F, Γ_F goes through a minimum when ε_0 is slightly above z_0. If $\varepsilon_0 = z_0$, then the threshold equals $\Gamma_F = 0.085 T_{N0}$, which corresponds to about 0.15% vanadium. This result is consistent with the experimental evidence[3,11] that the threshold impurity concentration lies somewhere between 0.1% and 0.2% vanadium. If a smaller value of g_0 is used, then the threshold will decrease like the square of g_0/T_{N0}. For example, if $g_0/T_{N0} = 0.60$ instead of 0.71, then $\Gamma_F = 0.061 T_{N0}$ corresponds to about 0.11% vanadium.

In order to determine the threshold concentration for other alloys, we would need to estimate the dependence of Γ on impurity concentration. Because the band-structure parameter α is large for manganese or rhenium alloys, Γ cannot be easily estimated from the enhancement of the Néel temperature with doping. So, while Γ_F may not sensitively depend on the band structure and dopant, the threshold concentration may vary greatly for different alloys.

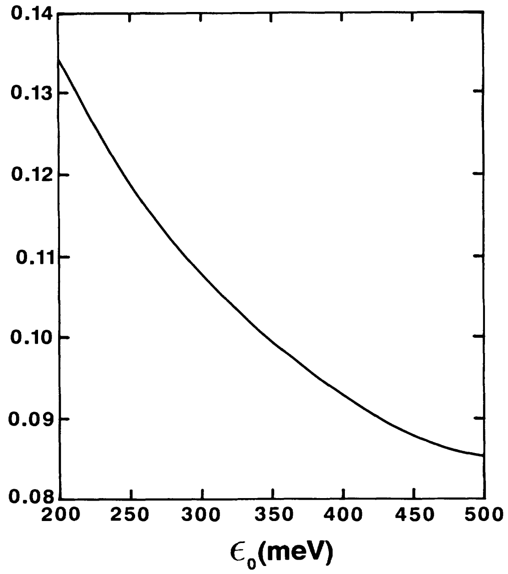

FIG. 6. Threshold impurity potential Γ_F normalized by T_{N0} vs the cutoff energy, with all parameters the same as in Fig. 4. A vanadium concentration of 0.2% corresponds to $\Gamma_F/T_{N0} \approx 0.115$.

For a fixed value of ε_0 and g_0/T_{N0}, Γ_F/T_{N0} is a decreasing function of z_0. For example, if $\varepsilon_0 = 500$ meV, then Γ_F/T_{N0} decreases from 0.085 to 0.078 as z_0 increases from 500 to 600 meV. This weak dependence arises from the function G, which decreases as z_0 increases.

Because we have assumed that T_{N0}/z_0 is small, it is difficult to extract the limit of vanishing z_0 from Eqs. (53) and (54). In the first-order regime, λ' must lie between λ'_F and $\lambda'_c = \frac{1}{2}$. So, using Eq. (21) for λ'_F, we conclude that

$$\lambda' - \lambda'_F < \frac{8\pi^2}{7}\left[\frac{T_{N0}}{z_0}\right]^2 \frac{(1-4\lambda G)^2}{\lambda^2\zeta(3)} . \tag{55}$$

Therefore Eq. (53) implies that Γ_F/T_{N0} vanishes like $1-4\lambda G$ as z_0 tends to zero. From Eq. (32) for g_0, we find that $(g_0/T_{N0})^2$ also vanishes like $1-4\lambda G$ as $z_0 \to 0$. On the other hand, Eq. (54) implies that the ratio of Γ_F/T_{N0} and $(g_0/T_{N0})^2$ is finite in the limit of vanishing z_0.

Physically, these results are reasonable: As z_0 decreases, the SDW becomes commensurate, the first-order transition in pure chromium becomes weaker, and the threshold concentration of impurities must tend to zero. In the previous section, we discovered that the threshold λ'_F approaches the critical value of $\frac{1}{2}$ as $z_0 \to 0$. Hence a first-order transition survives within a shrinking window of λ' as z_0 decreases. This result is confirmed by Eq. (55), where the numerator $(1-4\lambda G)^2$ vanishes faster than the denominator (which would really vanish like z_0 if we had not evaluated the integrals to lowest order in $1/z_0$).

VI. CONCLUSION AND DISCUSSION

In this paper we have evaluated the threshold concentration of impurities required to destroy the first-order transition in chromium. Because the first-order transition in pure chromium is weak, only a very small concentration of impurities is required to drive the system second order. The threshold value decreases as the SDW becomes commensurate with the lattice, and the phase transition of pure chromium becomes more weakly first order.

The most remarkable result of our work is that *impurity scattering alone can explain the very low impurity threshold.* As mentioned in the last section, we have included only one of the many possible effects of impurities on the band structure of chromium. Although the change in T_{N0} cancels out of our final result for Γ_F, the other changes in band structure may not be negligible. In addition, we have assumed that the non-nested contributions to Γ_F may be neglected. Because $\gamma = z_0/2\pi T_{N0} \approx 3$ is not very large, however, the non-nested contributions may also affect Γ_F. While the change in band structure and the higher-order terms in $1/z_0$ may shift Γ_F by as much as 50% from our prediction, we still expect that the threshold impurity concentration lies somewhere between 0.1% and 0.2%.

Unfortunately, most experimental work has been done with samples containing more than 0.2% impurities. In order to test the prediction of this work, we encourage experimentalists to fabricate and study samples with less than 0.2% impurities. While the elasticity measurements of Fawcett *et al.*[3] and the neutron-scattering measurements of Lebech and Mikke[11] indicate that the threshold probably lies between 0.1% and 0.2%, more work is needed to pinpoint the threshold value.

When Γ is below the threshold value, the jump $\tilde{g}_0$ in the order parameter at T_N should scale simply like

$$\tilde{g}_0^2 = g_0^2 \left[1 - \frac{\Gamma}{\Gamma_F} \right] , \tag{56}$$

which vanishes when $\Gamma = \Gamma_F$. This scaling might be observed by measuring the jump in the magnetic moment with neutron scattering.

Clearly, chromium is a complex and fascinating system that holds many surprises to come. In the future we hope to build upon this work by studying the dynamics of doped chromium in its paramagnetic state.

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APPENDIX A

In this appendix we evaluate the summations and integrations that are required to perform the calculations in the text. Whenever the summation over the Matsubara frequency and the integral over energy z do not commute, the Matsubara summation is performed first. Of course, δ_n and $\tilde{g}_n$ are evaluated by performing the energy integral for a fixed Matsubara frequency ω_n.

In order to evaluate the denominator D of δ, we use

$$\begin{aligned} I_1 &= \frac{\nu'}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_{b+})(i\omega_n - \varepsilon_{b-})} \\ &= 2\lambda' \int_{-\infty}^{\infty} dz \left[-\frac{f(-z)}{z_0} + \frac{f(-z+z_0)}{z_0} \right] \\ &= -2\lambda' , \end{aligned} \tag{A1}$$

where

$$f(z) = \frac{1}{e^{\beta z} + 1} \tag{A2}$$

is the Fermi function. It is essential that the Matsubara sum in Eq. (A1) be performed first. If the energy integral had been performed before the sum over n, I_1 would vanish.

The next two integrals include non-nested contributions and are evaluated exactly:

$$\begin{aligned} I_2 &= -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_a)(i\omega_n - \varepsilon_{b+})(i\omega_n - \varepsilon_{b-})} \\ &= -\frac{2}{z_0} \left[1 - \lambda \ln \left[\frac{T}{T_{N0}} \right] \right] + \frac{8\lambda}{z_0} G(T) , \end{aligned} \tag{A3}$$

$$\begin{aligned} I_3 &= -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_a)(i\omega_n - \varepsilon_{b+})} \\ &= 1 - \lambda \ln \left[\frac{T}{T_{N0}} \right] , \end{aligned} \tag{A4}$$

where T_{N0} is given by Eq. (14) and is a function of $G(T_{N0})$. If $z_0 = 0$ and $T = T_{N0}$, then $G = 1/4\lambda$ and $I_2 = 0$.

The non-nested contributions to the remaining integrals are neglected. So, to lowest order in $1/z_0$,

$$\begin{aligned} I_4 &= -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_a)^3 (i\omega_n - \varepsilon_{b+})^3} \\ &= \frac{3\lambda\pi T}{4} \sum_{n=0}^{\infty} \frac{1}{\omega_n^5} = \frac{93\lambda}{128} \frac{\zeta(5)}{(\pi T)^4} , \end{aligned} \tag{A5}$$

$$\begin{aligned} I_5 &= -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_a)(i\omega_n - \varepsilon_{b+})^2 (i\omega_n - \varepsilon_{b-})} \\ &= -\frac{\lambda\pi T}{2} \sum_{n=0}^{\infty} \frac{1}{\omega_n(\omega_n^2 + z_0^2/4)} \\ &\approx -\frac{1}{z_0^2} , \end{aligned} \tag{A6}$$

$$\begin{aligned} I_6 &= -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_a)^2 (i\omega_n - \varepsilon_{b+})^2 (i\omega_n - \varepsilon_{b-})} \\ &= \frac{\lambda\pi T z_0}{4} \sum_{n=0}^{\infty} \left[\frac{1}{\omega_n^3(\omega_n^2 + z_0^2/4)} + \frac{1}{2} \frac{1}{\omega_n(\omega_n^2 + z_0^2/4)^2} \right] \\ &\approx \frac{7\lambda}{8(\pi T)^2} \frac{\zeta(3)}{z_0} , \end{aligned} \tag{A7}$$

$$\begin{aligned} I_7 &= -\frac{\nu}{N} T \sum_{n,\mathbf{k}} \frac{1}{(i\omega_n - \varepsilon_a)^2 (i\omega_n - \varepsilon_{b+})^2} \\ &= -\lambda\pi T \sum_{n=0}^{\infty} \frac{1}{\omega_n^3} = -\frac{\lambda}{(\pi T)^2} \frac{7\zeta(3)}{8} , \end{aligned} \tag{A8}$$

where the Riemann zeta function $\zeta(n)$ is defined by

$$\sum_{p=1}^{\infty} \frac{1}{p^n} = \zeta(n) , \tag{A9}$$

$$\sum_{p=0}^{\infty} \frac{1}{(2p+1)^n} = \left[1 - \frac{1}{2^n} \right] \zeta(n) . \tag{A10}$$

Note that $\zeta(2) = \pi^2/6$, $\zeta(3) \approx 1.202$, $\zeta(4) = \pi^4/90$, and $\zeta(5) \approx 1.037$.

APPENDIX B

In this appendix we evaluate the A_3 term in the free-energy expansion of Sec. III. To evaluate the fifth-order term in the self-consistent equation for g, we must first calculate the fourth-order term in the self-consistent equation for δ. After expanding $1/\mathcal{D}$ in powers of g^2 and using the results in Appendix A, we find that

$$\delta = -\frac{2}{\lambda}\frac{\lambda'}{1-2\lambda'}\frac{g^2}{z_0}\left[1-\lambda\ln\left[\frac{T}{T_{N0}}\right]\right] + 8G\frac{\lambda'}{1-2\lambda'}\frac{g^2}{z_0} + \frac{7\zeta(3)}{4\pi^2}\frac{\lambda'}{1-2\lambda'}\frac{g^4}{T^2 z_0} . \tag{B1}$$

Because $\ln(T/T_{N0})$ is itself of order g^2, the term proportional to $g^2\ln(T/T_{N0})$ is actually of order g^4. Since $1/(1-2\lambda')$ is of order $(z_0/T_{N0})^2$, all the contributions in Eq. (B1) are of order z_0.

Expanded to order g^5 and expressed in terms of δ, the self-consistent equation for g is

$$\lambda\ln\left[\frac{T}{T_{N0}}\right] = -\frac{2}{z_0}\left[1-\lambda\ln\left[\frac{T}{T_{N0}}\right]\right]\delta + \frac{8\lambda}{z_0}G\delta - \frac{7\lambda\zeta(3)}{8(\pi T)^2}g^2 + \frac{7\lambda\zeta(3)}{2(\pi T)^2 z_0}\delta g^2 + \frac{93\lambda\zeta(5)}{128(\pi T)^4}g^4 , \tag{B2}$$

where $\zeta(5)\approx 1.04$. Substituting for δ and solving for A_3, we finally obtain

$$A_3 = \frac{16}{3}\left[\frac{\lambda'}{1-2\lambda'}\right]^2\frac{(1-4\lambda G)^2}{\lambda^2 z_0^4} + \frac{7\zeta(3)}{12\pi^2}\frac{\lambda'}{1-2\lambda'}\frac{1-12\lambda G}{T^2 z_0^2} - \frac{31\zeta(5)}{256\pi^4}\frac{\lambda}{T^4} , \tag{B3}$$

which is positive in the first-order regime.

APPENDIX C

In this appendix we evaluate the modified order parameters and frequencies in the presence of impurities. To order g^2, Eq. (34) implies that

$$\tilde{\delta}_n = \delta + \frac{i\Gamma}{4}g^2\frac{\operatorname{sgn}(\omega_n)}{\omega_n(\omega_n+iz_0/2)} . \tag{C1}$$

After expanding $1/\mathcal{D}$ to order g^2, we also find that

$$\tilde{g}_n = g\left[1-\frac{\Gamma}{4}\left[\frac{1}{\omega_n}+\frac{1}{\omega_n+iz_0/2}\right]\operatorname{sgn}(\omega_n)\right] + \frac{i\Gamma}{4}g\delta\frac{\operatorname{sgn}(\omega_n)}{\omega_n(\omega_n+iz_0/2)} + \frac{\Gamma}{8}g^3\frac{\operatorname{sgn}(\omega_n)}{\omega_n^3} . \tag{C2}$$

Since δ is formally of order z_0, the second term in Eq. (C2) is formally of order 1. In order to obtain the correct $z_0=0$ limit of the self-consistent equations, we have retained the non-nested contribution of order $g\Gamma/z_0$. Although our expressions for $\tilde{g}_n$ and $\tilde{\delta}_n$ disagree with the results of YS, they correctly reduce to the results of Zittartz when $z_0=0$.

To zeroth order in g, the frequencies $\tilde{\omega}_n^a$ and $\tilde{\omega}_n^b$ are given by

$$\tilde{\omega}_n \equiv \omega_n + \frac{\Gamma}{2}\operatorname{sgn}(\omega_n) . \tag{C3}$$

But to order g^2,

$$\tilde{\omega}_n^a = \tilde{\omega}_n - \frac{\Gamma}{4}g^2\frac{\operatorname{sgn}(\omega_n)}{\omega_n^2} , \tag{C4}$$

$$\tilde{\omega}_n^b = \tilde{\omega}_n - \frac{\Gamma}{8}g^2\frac{\operatorname{sgn}(\omega_n)}{\omega_n^2} \tag{C5}$$

differ by a term of order $\Gamma g^2/T^2$.

APPENDIX D

The self-consistent equation for the CDW order parameter g is given by Eq. (51) in the text. In this appendix we evaluate the various contributions to this relation to linear order in Γ and to second order in g.

Expanding the $\tilde{g}_n/g$ contribution to order g^2 and to order Γ, we find that

$$\begin{aligned}
-\frac{\nu}{N}T\sum_{n,\mathbf{k}}\frac{\tilde{g}_n}{g}&\frac{1}{(i\tilde{\omega}_n^a-\varepsilon_a)(i\tilde{\omega}_n^b-\varepsilon_{b+})}\\
=\lambda T\sum_n\int_{-\infty}^{\infty}dz&\left[1-\frac{\Gamma}{4}\frac{\operatorname{sgn}(\omega_n)}{\omega_n}+\frac{i\Gamma}{4}\delta\frac{\operatorname{sgn}(\omega_n)}{\omega_n(\omega_n+iz_0/2)}+\frac{\Gamma}{8}g^2\frac{\operatorname{sgn}(\omega_n)}{\omega_n^3}\right]\frac{1}{\omega_n^2+z^2}\\
&\times\left[1-\frac{i\Gamma}{2}\frac{\operatorname{sgn}(\omega_n)}{i\omega_n-z}+\frac{i\Gamma}{4}g^2\frac{\operatorname{sgn}(\omega_n)}{\omega_n^2(i\omega_n-z)}\right]\left[1-\frac{i\Gamma}{2}\frac{\operatorname{sgn}(\omega_n)}{i\omega_n+z}+\frac{i\Gamma}{8}g^2\frac{\operatorname{sgn}(\omega_n)}{\omega_n^2(i\omega_n+z)}\right]\\
=1-\lambda\ln\left[\frac{T}{\tilde{T}_{N0}}\right]&-\frac{3\pi\lambda\Gamma}{16}\left[\frac{1}{T}-\frac{1}{T_{N0}}\right]+\frac{\pi\lambda z_0\Gamma}{4}\delta T\sum_{n=0}^{\infty}\frac{1}{\omega_n^2(\omega_n^2+z_0^2/4)}+\frac{5\pi\lambda\Gamma}{8}g^2T\sum_{n=0}^{\infty}\frac{1}{\omega_n^4}\\
=1-\lambda\ln\left[\frac{T}{\tilde{T}_{N0}}\right]&+\frac{3\pi\lambda\Gamma}{16T^2}(T-T_{N0})-\frac{\pi\Gamma}{4Tz_0^2}g^2\frac{\lambda'}{1-2\lambda'}+\frac{5\pi\lambda\Gamma}{768T^3}g^2 ,
\end{aligned} \tag{D1}$$

which uses Eq. (C2) for $\tilde{g}_n$ and Eqs. (C3)–(C5) for $\tilde{\omega}_n^a$ and $\tilde{\omega}_n^b$. This integral is evaluated by using the fact that Γ is small compared to any Matsubara frequency $\omega_n=\pi T(2n+1)$. Because $T-T_{N0}$ is proportional to g^2, the third term in the last line of Eq. (D1) is proportional Γg^2.

Similarly, the g^2 contribution to Eq. (51) is

$$-\frac{\nu}{N}T\sum_{n,\mathbf{k}}\frac{\tilde{g}_n^3}{g}\,\frac{1}{(i\tilde{\omega}_n-\varepsilon_a)^2(i\tilde{\omega}_n-\varepsilon_{b+})^2}=-\frac{7\lambda\zeta(3)}{8(\pi T)^2}g^2+g^2\lambda\Gamma T\sum_n\int_{-\infty}^{\infty}dz\left[\frac{3}{4}\,\frac{\operatorname{sgn}(\omega_n)}{\omega_n(\omega_n^2+z^2)^2}+2\frac{\operatorname{sgn}(\omega_n)\omega_n}{(\omega_n^2+z^2)^3}\right]$$

$$=-\frac{7\lambda\zeta(3)}{8(\pi T)^2}g^2+\frac{3\pi\lambda\Gamma}{128T^3}g^2\,, \tag{D2}$$

which again uses Eq. (C2) for $\tilde{g}_n$.

Finally, the δ integral is

$$-\frac{\nu}{N}T\sum_{n,\mathbf{k}}\frac{\tilde{g}_n}{g}\tilde{\delta}_n\frac{1}{(i\tilde{\omega}_n-\varepsilon_a)(i\tilde{\omega}_n-\varepsilon_{b+})(i\tilde{\omega}_n-\varepsilon_{b-})}$$

$$=-\frac{2\lambda\pi T}{z_0}g^2\sum_n\frac{\operatorname{sgn}(\omega_n)}{\omega_n}\left[1-\frac{\Gamma\operatorname{sgn}(\omega_n)}{2\omega_n}\right]\left[1-\frac{\Gamma\operatorname{sgn}(\omega_n)}{4\omega_n}\right]\frac{\lambda'}{1-2\lambda'}\,\frac{1}{z_0}\left[-\frac{2}{\lambda}+\frac{\pi\Gamma}{8T}+\frac{2\alpha\Gamma}{T}\right]$$

$$=\frac{4}{\lambda z_0^2}g^2\frac{\lambda'}{1-2\lambda'}\left[1-\lambda\frac{\pi}{16}\,\frac{\Gamma}{T}-2\alpha\lambda\frac{\Gamma}{T}\right]\,, \tag{D3}$$

where the logarithmically divergent sum over ω_n is cut off at $\varepsilon_0/2\pi T$ and Eq. (C1) is used for $\tilde{\delta}_n$.

Adding the contributions of Eqs. (D1)–(D3) yields the result given in Eq. (52).

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