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IMPURITY EFFECTS ON THE MAGNETIC ORDERING IN CHROMIUM

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It is well-known that impurities profoundly alter the magnetic properties of chromium. While vanadium impurities suppress the Néel temperature T_N , manganese impurities enhance T_N substantially. As evidenced by neutron scattering experiments, doping with as little as 0.2% vanadium changes the transition from weakly first order to second order. Young and Sokoloff explained that the first-order transition in pure chromium is caused by a charge-density wave which is the second harmonic of the spin-density wave. By examining the subtle balance between the spin-density and charge-density wave terms in the mean-field free energy, we find that the first-order transition is destroyed when the vanadium concentration exceeds about 0.15%, in agreement with experiments.

Neutron scattering^{1,2} and elastic strain^{3,4} measurements clearly indicate that the antiferromagnetic phase transition of chromium at $T_N \approx 310$ K is weakly first order. Below T_N , the spin-density wave⁵ (SDW) in chromium is incommensurate with the lattice.^{6,7} It is well-known that impurities have a profound effect on the magnetic ordering in chromium. 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 By examining the subtle balance between competing terms in the free energy, we find that the mean-field theory originally developed by Zittartz⁸ and Young and Sokoloff⁹ (YS) 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 chromium¹⁰ consists of an electron "jack" and a slightly larger hole "octahedron," which are imperfectly nested by the wavevector $Q = 2\pi(1 + \delta)/a$, where a is the lattice constant of chromium. Because $\delta < 0$, the SDW with wavevector Q is incommensurate with the lattice. While doping with vanadium enlarges the hole surface and increases $|\delta|$, doping with manganese enlarges the electron surface and reduces $|\delta|$.

Because $Q \neq 2\pi/a$, the band structure of chromium actually contains one electron and two hole surfaces.⁵ Due to 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 wavevector $2Q$. The SDW is induced by the Coulomb attraction λ between quasiparticles on the electron and holes surfaces,⁹ which allows the electrons and holes to move coherently through the metal. The CDW, on the other hand, is induced by the Coulomb repulsion λ' between quasiparticles on the two hole surfaces. According to the mean-field theory of YS, the CDW is responsible for the first-order transition in pure chromium.

Although weak, the first-order transition in pure chromium was clearly observed by Arrott, Werner, and Kendrick,¹ who measured a discontinuous change at T_N in the neutron-scattering intensity at the wavevector \vec{Q} . 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 intensity² at \bar{Q} . The discontinuity in the thermal expansivity is smaller³ in a sample with 0.1% vanadium and vanishes in a sample with 0.2% vanadium. In neutron scattering measurements, Lebech and Mikke¹¹ 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%.

Because YS only included a subset of the impurity corrections which contribute to the mean-field free energy, their numerical estimates for the threshold impurity concentration disagreed with experiment. We have reexamined the subtle balance between all of the impurity corrections to the mean-field free energy. In order to analyze the mean-field equations for the charge-density and spin-density waves 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 $\Gamma \approx 3$ meV, $T_N \approx 27$ meV, and $z_0 \approx 500$ meV, the energy scales are fairly well separated. We also assume that the wavevector Q of the SDW is not affected by doping.

Since the band structure of chromium contains two hole and one electron bands, the Green's function $\underline{G}(\vec{k}, i\omega_n)$ is a 6×6 matrix (accounting for the spin). The self-consistent equations for the SDW and CDW order parameters were originally discovered by YS:

$$g = -\frac{\nu}{N} T \sum_{n, \vec{k}} \frac{i\omega_n - \epsilon_b(\vec{k}) + \delta}{det} g, \quad (1)$$

$$\delta = -\frac{\nu'}{N} T \sum_{n, \vec{k}} \frac{(i\omega_n - \epsilon_a(\vec{k}))\delta + g^2}{det}, \quad (2)$$

where ν is the electron-hole Coulomb interaction, ν' is the hole-hole Coulomb interaction, and det is the determinant of the 6×6 inverse Green's function. 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.(2) with $g = 0$. For any other value of ν' , both ν and ν' must be nonzero to support a CDW.

Using the quasiparticle energies originally proposed by Falicov and Penn¹⁰, we have evaluated δ to order g^2 :

$$\delta = -2 \frac{\lambda'}{z_0 \lambda} \frac{g^2}{1 - 2\lambda'} (1 - 4\lambda G), \quad (3)$$

where $\lambda = N(0)\nu/2$ and $\lambda' = N(0)\nu'/2$ are scaled by the density-of-states $N(0)$. The function $G(T, z_0)$ reflects the non-nested contributions to the CDW and vanishes as $z_0 \rightarrow \infty$. When $\lambda' = \lambda'_c \equiv 1/2$, the self-consistent equation for δ has a nontrivial solution even when $g = 0$. So at λ'_c , a CDW instability occurs. 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.

To expand the self-consistent equation for g , we neglect contributions of order $(T_N/z_0)^2$ and higher to the self-consistent equation:

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

where T_{N0} is the second-order transition temperature. When G is neglected, this expression agrees with the result of YS. The transition is first-order if this expression has a non-trivial

solution when $T > T_{N0}$: when the second term in brackets exceeds the first. Therefore, the threshold value for λ' , above which the transition becomes first order, is given by

$$\frac{\lambda'_F}{1 - 2\lambda'_F} = \frac{7}{32\pi^2} \frac{\lambda^2 \zeta(3)}{(1 - 4\lambda G)^2} \left(\frac{z_0}{T_{N0}} \right)^2 \gg 1. \quad (5)$$

Based on the model band structure we have estimated that $G \approx 0.30$ and λ'_F is close to 0.39. Hence, 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 $\lambda'_c = 0.5$.

Generally, the phase transition is weakly first order when λ' just exceeds λ'_F . The actual value of λ' can be evaluated in terms of the jump g_0 in the order parameter at the first-order transition. By expanding the free energy to order g^6 , we find that¹²

$$\left(\frac{g_0}{T_{N0}} \right)^2 = \left(\frac{z_0}{T_{N0}} \right)^2 \frac{49\zeta(3)^2 \lambda^2 (\lambda' - \lambda'_F)}{2(1 - 4\lambda G)} \left\{ 98\lambda\zeta(3)^2 - 31\zeta(5)(1 - 4\lambda G) \right\}^{-1}. \quad (6)$$

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.

In order to study the effects of impurity scattering, we have generalized¹² the formalism of Zittartz,⁸ which was originally designed for a metal with only two bands. For small concentrations of impurities, the modified Néel temperature is given by $\tilde{T}_N = T_N - 3\pi\Gamma/16$, where Γ is the energy width produced by scattering. 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_N is fixed). Although impurity scattering always suppresses the Néel temperature, the decrease of z_0 and increased commensurability of the SDW with manganese doping result in a net increase in the Néel temperature.

We have also examined the effects of impurities on the CDW and SDW order parameters. Since impurity scattering breaks electron-hole pairs, impurity scattering suppresses both the SDW order parameter g and the CDW order parameter $\delta \propto g^2$. However, because our theory neglects the change in band-structure with doping, we cannot predict the effects of manganese doping on the SDW and CDW order parameters. Further experiments are required to determine the behavior of the order parameters for small concentrations of manganese.

After a lengthy calculation,¹² we have generalized Eq.(4) in the presence of impurities. Of course, the threshold value for Γ is obtained by setting the coefficient of g^2 equal to zero. After linearizing in $\lambda' - \lambda'_F$, we find that

$$\frac{\Gamma_F}{T_{N0}} = 12\pi \left(\frac{7\lambda\zeta(3)}{\pi^2} \right)^2 \left(\frac{z_0}{T_{N0}} \right)^2 \frac{\lambda' - \lambda'_F}{1 - 4\lambda G} \left\{ 84\zeta(3)(3(1 + 4\lambda G) + \lambda) - 23\pi^2(1 - 4\lambda G) \right\}^{-1}, \quad (7)$$

As expected, the threshold value decreases as $\lambda' - \lambda'_F$ decreases.

Finally, we can use Eq.(6) to eliminate the Coulomb interaction λ' in favor of the experimentally measured 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 . Using the experimental value $g_0/T_{N0} = 0.71$, we find that the threshold Γ_F/T_{N0} lies between 0.11 and 0.09 depending on the energy cutoff. These values for Γ_F correspond to between 0.13 and 0.18% vanadium, which is in good agreement with experiments.

Because the first-order transition of pure chromium is weak, only a very small concentration of impurities is required to drive the system second order. Since the threshold λ'_F

approaches the critical value of $1/2$ as $z_0 \rightarrow 0$, the first-order transition survives within a shrinking window of λ' as z_0 decreases. Hence, the threshold Γ_F decreases as the SDW becomes commensurate with the lattice.

The most astonishing result of our work is that *impurity scattering alone can explain the very low impurity threshold*. Our mean-field calculation neglects the complex effects of impurities on the band-structure parameters like z_0 , the density-of-states, and the Coulomb interactions. We have also assumed that the non-nested contributions to Γ_F may be neglected. While the change in band structure and the higher-order terms in T_N/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 Mikke¹¹ indicate that the threshold probably lies between 0.1 and 0.2%, more work is needed to pinpoint the threshold value.

Clearly, chromium is a complex and fascinating system which 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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References

1. A. Arrott, S.A. Werner, and H. Kendrick, *Phys. Rev. Lett.* **14** (1965) 1022.
2. D.R. Noakes, T.M. Holden, and E. Fawcett, *J. Appl. Phys.* **67** (1990) 5262.
3. E. Fawcett, R.B. Roberts, R. Day, and G.K. White, *Europhys. Lett.* **1** (1986) 473.
4. P.C. de Carmargo, E.P. Castro, and E. Fawcett, *J. Phys. F* **18** (1988) L219.
5. P.A. Fedders and P.C. Martin, *Phys. Rev.* **143** (1966) 245.
6. W.C. Koehler, R. Moon, A.L. Trego, and A.R. MacKintosh, *Phys. Rev.* **151** (1966) 405.
7. S.H. Liu, *Phys. Lett.* **27A** (1968) 493.
8. J. Zittartz, *Phys. Rev.* **164** (1967) 575.
9. C.Y. Young and J.B. Sokoloff, *J. Phys. F* **4** (1974) 1304.
10. L.M. Falicov and D.R. Penn, *Phys. Rev.* **158** (1967) 476.
11. B. Lebech and K. Mikke, *J. Phys. Chem. Solids* **33** (1972) 1651.
12. R.S. Fishman and S.H. Liu, *Phys. Rev. B* **45** (1992) 12306.