Pressure-Tuned Spin and Charge Ordering in an Itinerant Antiferromagnet

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Elemental chromium orders antiferromagnetically near room temperature, but the ordering temperature can be driven to zero by applying large pressures. We combine diamond anvil cell and synchrotron x-ray diffraction techniques to measure directly the spin and charge order in the pure metal at the approach to its quantum critical point. Both spin and charge order are suppressed exponentially with pressure, well beyond the region where disorder cuts off such a simple evolution, and they maintain a harmonic scaling relationship over decades in scattering intensity. By comparing the development of the order parameter with that of the magnetic wave vector, it is possible to ascribe the destruction of antiferromagnetism to the growth in electron kinetic energy relative to the underlying magnetic exchange interaction.

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Electronic, magnetic and optical properties of itinerant ferromagnets are being studied by an increasing number of researchers, as a result of the increasing interest in discovering and developing new materials with exotic properties [3,4,5]. The interest in these materials is due to their potential for application in a variety of fields, such as magnetism, electronics, and energy conversion.

In order to understand the behavior of these materials, it is important to study the relationship between the magnetic and electronic properties. This relationship is often referred to as the magnetic-mechanical effect, and it is observed in a variety of materials, including ferromagnets, antiferromagnets, and ferrimagnets [6,7]. The magnetic-mechanical effect is a consequence of the coupling between the magnetic and electronic properties, and it is observed in a variety of materials, including ferromagnets, antiferromagnets, and ferrimagnets [6,7].

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section [16], we are able to calculate the $Q$ of measuring the order parameters. Furthermore, the presence of the domain distribution with pressure underscores the form factor [18] and the appropriate strain wave cross section [18], indicating that the coupling of the spins to the charge is a function of pressure, $T = 8$ K. Data have been normalized to the (2,0,0) lattice Bragg peak intensity and account for $Q$- and $S$-domain distributions. Both intensities are suppressed exponentially with the BCS form $I_x \propto \exp(C_\Delta a/\Delta_0)$, where $\Delta_0 = 2.8820 \text{ Å}$ is the lattice constant at ambient $P$ and 8 K; $C_{\text{SDW}} = 227 \pm 10$, $C_{\text{CDW}} = 457 \pm 25$. The $I_{\text{SDW}} \propto I_{\text{CDW}}$ scaling between the CDW and SDW intensities at $T = 8$ K is consistent with scaling seen at ambient pressure where $T$ is varied [16].

We find that the longitudinal phase is completely suppressed above $P = 1$ GPa at $T = 8$ K, so that all high-pressure measurements presented here are made in the transverse phase. Therefore, it is necessary to measure two inequivalent SDW reflections [such as (1,0, ±δ) and (0,1, ±δ)] in order to determine the $S$-domain distribution. The SDW ordered moment is then calculated from the equation

$$I_{\text{SDW}}/I_{\text{Lattice}} = (h\omega/m_\text{e}c^2)^2(f_m/f)^2(\mu/N)^2, \tag{1}$$

where $h\omega$ is the x-ray energy, $f_m$ and $f$ are the magnetic [17] and atomic [18] form factors, $N$ is the number of electrons per site, $\mu$ is the (rms) ordered moment per atom in units of $\mu_B$ [16], and $I_{\text{SDW}}$ and $I_{\text{Lattice}}$ are the (properly normalized) SDW and lattice diffraction intensities. Our measured ordered moment at ambient $P$ is $0.39 \pm 0.02 \mu_B$, consistent with the accepted value of $\mu_0 = 0.41$ [16].

We plot in Fig. 2(b) the evolution of the SDW and CDW diffraction intensities with $P$ at $T = 8$ K. Both order parameters are seen to scale exponentially with pressure over the entire measurement range. The quadratic scaling between $I_{\text{CDW}}$ and $I_{\text{SDW}}$ holds as a function of pressure, indicating that the coupling of the spins to the charge is

FIG. 2 (color online). (a) CDW $Q$-domain distributions for samples at different pressures and 8 K; ambient $P$ data were taken at 130 K in the transverse phase to be consistent with the high-pressure points. (b) SDW and CDW diffraction intensities $I_{\text{SDW}} = I_{(1,0,0)}/I_{(2,0,0)}$ and $I_{\text{CDW}} = I_{(2,0,0)}/I_{(2,0,0)}$ as a function of pressure at $T = 8$ K. Data have been normalized to the (2,0,0) lattice Bragg peak intensity and account for $Q$- and $S$-domain distributions. Both intensities are suppressed exponentially with the BCS form $I_x \propto \exp(C_\Delta a/\Delta_0)$, where $\Delta_0 = 2.8820 \text{ Å}$ is the lattice constant at ambient $P$ and 8 K; $C_{\text{SDW}} = 227 \pm 10$, $C_{\text{CDW}} = 457 \pm 25$. The $I_{\text{SDW}} \propto I_{\text{CDW}}$ scaling between the CDW and SDW intensities at $T = 8$ K is consistent with scaling seen at ambient pressure where $T$ is varied [16].

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not altered by varying the lattice constant. The exponential dependence of the ordered magnetic moment on pressure can be understood within the framework of the two band model of a nested SDW, which for the case of perfect nesting is analogous to a BCS superconductor [8]. To the extent that the exchange potential between the two nested sheets of Fermi surface is a constant, the model predicts that \( \mu \propto g_0 \), where \( 2g_0 \) is the energy gap responsible for eliminating the magnetic Fermi surfaces [8]. We therefore apply the expression for the gap [8]

\[
g_0 \propto \exp(-2\pi^2 v/\gamma^2 V k^2) \equiv \exp(-1/\lambda), \tag{2}
\]

to the experimentally determined ordered moment. Here \( \gamma \) is an average exchange integral, \( V \) is an average Coulomb potential, \( 4\pi k^2 \) is the Fermi surface area of the magnetic bands, and \( v \) is an average Fermi velocity. Comparing our data to Eq. (2) we see that \( 1/\lambda \), the ratio of kinetic energy \( t = v/k^2 \) to exchange potential density \( J = \gamma^2 V \) in reciprocal space, varies linearly with \( P \). The exponential decrease in ordered moment with pressure is consistent with the similar decrease in \( T_N \propto \exp(C_T \Delta a/a_0) \) with \( C_T = 93 \) [13]. We conclude that the suppression of antiferromagnetic order with pressure at the approach to the quantum critical point is described simply by a BCS-like linear relationship between \( T_N \) and \( g_0 \).

Pressure can suppress the gap \( g_0 \) principally through either the magnetic exchange coupling or the Fermi surface geometry of the magnetic bands. We separate these effects by studying the \( P \) dependence of the SDW wave vector \( Q \), which reflects the evolution of the band structure and the nesting condition. We compare in Fig. 3(a) the \( P \) dependence of \( Q \) at low \( T \) and its \( T \) dependence at ambient \( P \). \( Q(P) \) appears to flatten off with increased pressure, approaching a constant for \( P \geq 4 \) GPa. Given that the observed exponential dependence of \( \mu \) on \( P \) continues to at least 7.2 GPa, this demonstrates that the change in \( Q \) is not directly related to the evolution of \( g_0 \propto \exp(-1/\lambda) \). Changes in \( Q \) at \( T = 0 \) reflect changes in the geometry of the underlying paramagnetic nested Fermi surfaces, resulting from a redistribution of electrons in reciprocal space; for a rigid band structure \( Q \) would remain constant with pressure. The data show that the geometry of the nesting bands is essentially pressure independent, approaching the rigid limit for \( \Delta a/a_0 > 1\% \).

It is important to consider the possibility that imperfect nesting may alter the physics. In such a case, the spin response function at \( \chi_0(q = Q) \) would exhibit a broad maximum rather than a singular cusp [20], and \( g \) would be renormalized away from \( g_0 \) [9]. However, this posited renormalization is inconsistent with the observed exponential decrease in \( g \) with pressure, indicating that the gigapascal pressures applied in our experiment do not warp the band structure to the extent of significantly affecting the nesting condition.

FIG. 3 (color online). (a) Evolution of the SDW wave vector \( Q \) [in units of \( 2\pi/a(P) \)] with temperature and pressure. \( Q \) becomes independent of \( P \) at the approach to the quantum phase transition. \( T \) dependence at ambient \( P \) (blue) and \( P \) dependence at 92 K (gray) were measured with energy dispersive x-ray diffraction [15]; \( P \) dependence at 8 K (red) was measured with a monochromatic technique. Solid lines are guides to the eye. (b) Pressure (red) and vanadium doping (blue) track until disorder disrupts the BCS behavior. \( T_N \) for pure \( \text{Cr} \) under pressure is derived by using a linear relationship \( T_N(P) = \mu(P)/\mu_0 \propto 311 \) K, and from Ref. [13] with a pressure scale reduced by a factor of 1.24 to account for the difference in pressure calibrations. \( T_N \) for \( \text{Cr}_{1-x} \text{V}_x \) are collected from Refs. [11,12,21,22] and Refs. [15–17] within [12] for dopant concentrations up to \( x = 3.42\% \). The conversion between \( P \) and \( x \) is set by the collapse of all the doping data for \( x \leq 2.5\% \) onto the same exponential curve of pure \( \text{Cr} \) data under pressure, giving \( dP/dx = 1.99 \) GPa/\%.

The contrast between the physics of clean and disordered materials is brought into sharp relief in Fig. 3(b). It is possible to suppress \( T_N \) not only with pressure, but also by doping with \( \text{V} \) [11,21]. The two techniques track over a wide range, but chemical doping, which introduces both disorder and change in the average electron count, drives the system away from a BCS form for \( T_N \leq 2/5T_N(x = 0, P = 0) \). The simple description of the evolution of magnetism in terms of the BCS energy gap is cut off by disorder, hastening the onset of the proximate quantum phase transition. Furthermore, for 2.5% \( \text{V} \) doping (\( T_N = 125 \) K) the low-\( T \) value of \( Q \) moves to 0.922 and \( \mu \) is suppressed to 0.24\( \mu_0 \) [22]. By comparison, compressing pure \( \text{Cr} \) drives \( \mu \) to 0.24\( \mu_0 \) when \( Q = 0.9394 \), only 1/3 the change in \( Q \). The evolution of \( Q(x) \) for \( \text{Cr}_{1-x} \text{V}_x \) [22,23] does not level off for larger values of \( x \) as does \( Q(P) \). Therefore, we find that chemical doping in the form of deviations from stoichiometry alters \( \text{Cr} \)'s band structure to considerably larger degree than applying pressure. At a minimum this makes separating competing physical effects more difficult and at a maximum may point to the
mechanism by which deviations from pure BCS-like behavior ensue.

The direct measurement of the SDW and CDW order parameters at temperatures where thermal fluctuations are frozen out, combined with the flattening off of the SDW wave vector at the approach to the quantum critical point, reveal that it is the ratio of magnetic exchange to kinetic energy, \( \lambda = J/t \), which drives the quantum phase transition in pure Cr. A quantitative estimate for \( \lambda \) can be obtained from recalling that for three-dimensional Fermi liquids we expect the total kinetic energy of the electrons to scale like \( a^{-5} \), which increases strongly under pressure as a quantum confinement effect. From the data up to \( P = 7.2 \) GPa, the fractional change in the kinetic energy \( \Delta t/t_0 = -5\Delta a/a_0 = 0.06 \) which, together with the measured \( \Delta(1/\lambda) = 1.3 \), leads to \( \lambda = J/t \sim 0.05 \). We have assumed that the exchange interactions are not sensitive to the lattice constant, and indeed, if anything, they should become stronger with pressure, which would imply an even larger kinetic energy contribution to the change in \( \lambda \). In this picture, the magnetic order is destabilized by the increase in the kinetic energy due to quantum confinement.

Even with \( \lambda \) small, the spin interactions can be robust. Inelastic neutron scattering studies demonstrate that spin-spin correlations survive up to surprisingly high energies and temperatures [24], and the Hall coefficient retains a strong temperature dependence well above the Neél transition [11]. The intrinsic exchange-driven pairing potential is thus strong in Cr, but its ground state evolution still can be modeled by the BCS-like gap solution given the high density of carriers and consequent high degree of pair overlap [25]. Of course, the BCS form for the order parameter only approaches zero asymptotically. As with chemical doping [Fig. 3(b)], the curve is likely to turn over and assume a critical form at sufficiently large \( P \). Alternate broken symmetries such as superconductivity become a possibility if disorder is sufficiently weak, as does the survival of a purely second-order quantum phase transition, depending on the strength of the coupling of the harmonics to the primary SDW [10].

In summary, we have performed a direct study of spin and charge ordering in the stoichiometric itinerant antiferromagnet Cr as the magnetic order is suppressed with pressure. We find that this suppression is an effect of quantum confinement, the ground state evolves in accordance with the BCS weak-coupling theory, and the spin and charge degrees of freedom have a persistent harmonic relationship. The low-\( T \) behavior of the pure element differs dramatically from that of the family of doped systems approaching the quantum phase transition.

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[14] Miniature Cr single-crystals with a FWHM mosaicity varying from 0.05° to 0.18° were prepared from a large single-crystal wafer (Alfa Aesar, 99.996 + %) following procedures in Ref. [15]. A methanol/ethanol (4:1) mixture was used as the pressure medium. Gold was used as manometer \textit{in situ} with an uncertainty of 0.2 GPa. Energy dispersive x-ray diffraction was performed at the bending magnet beam line 16-BM-B of the Advanced Photon Source (APS), using a chemical-filter technique to resolve the CDW peak from the adjacent lattice peak [15]. High-resolution monochromatic x-ray diffraction was performed with focused 20-keV x rays at the undulator beam line 4-ID-D at the APS.