Persistence of atomic magnetism in the paramagnetic phase of chromium

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A temperature-dependent study of the Cr $3s$ x-ray-photoelectron-spectroscopy (XPS) line shape measured from Cr(001) is reported. As the temperature is raised from well below the Néel temperature T_N (311 K) to far above it ($\sim 3.3 T_N$), no variation of the $3s$ XPS line shape is observed. This invariance is insensitive to surface chemisorption, suggesting that the behavior is not determined by the enhanced Cr(001) surface magnetization. The results indicate that the atomic $3d$ spin density within 1 Å of the atomic center is the same in the antiferromagnetic (AF) and paramagnetic (PM) phases of Cr. No evidence is found for a theoretically predicted collapse of the atomic magnetic moment in PM Cr, or for the thermal population of spin fluctuations. The results are particularly striking, given the observation of the loss of AF order in Cr by valence-band photoemission. The local atomic $3d$ spin density therefore persists in the absence of short-range magnetic order within a range of ~ 6 Å.

I. INTRODUCTION

The nearly half-filled $3d$ band of Cr produces fascinating electronic and magnetic properties in the bulk metal and at Cr surfaces. An excellent review of these properties has been written by Fawcett.[1] Neutron-diffraction measurements[2–5] on Cr reveal the existence of a spin-density wave[6] (SDW) whose periodicity is incommensurate with the body-centered-cubic (bcc) crystal lattice. The SDW requires nearest-neighbor atoms to possess antiparallel magnetic moments μ. Its incommensurate periodicity causes the magnitude of these moments to vary sinusoidally:

$$\mu = \mu_0 \cos(\mathbf{Q} \cdot \mathbf{r}) . \tag{1}$$

Here, μ_0 is the maximum magnitude of μ; $\mu_0 = 0.59 \mu_B$. The periodicity of the SDW is given by the wave vector $\mathbf{Q}$, with $\mathbf{Q} = (1 \pm \delta)(2\pi/a)\langle 100 \rangle$. The value of δ indicates the deviation from commensurate periodicity; it is observed to be temperature dependent but is typically ~ 0.05.[2–5] The lattice constant a takes the value 2.884 Å. The root-mean-square (rms) value of the magnetic moment is $0.43 \mu_B$ in the SDW state.[2]

Very recently, the magnetic and electronic properties of Cr have been described in a "spin-split" formalism.[7] This theory, however, predicts the absence of real-space antiferromagnetic (AF) order in Cr. This prediction is in contradiction with angle-resolved photoelectron-spectroscopy (ARPES) studies[8–10] of Cr.

Chromium undergoes a first-order magnetic phase transition at the Néel temperature $T_N = 311$ K. Many macroscopic properties, such as the electrical resistivity, heat capacity, and thermal expansivity, exhibit singular behavior at T_N.[1] There exists a theoretical consensus[11–15] that the high-temperature paramagnetic (PM) phase of Cr does *not* consist of well-defined local atomic magnetic moments, but rather consists of essentially nonmagnetic atoms whose local spin density (i.e., magnetic

moments) may be thermally fluctuating in magnitude and direction. Figure 1 clarifies the distinction between "well-defined" local magnetic moments and the absence of such moments in a spin-fluctuation sense.[15] Figure 1 plots the free energy versus the magnitude of the atomic moment (represented theoretically as the "local band splitting," or "local exchange field") in two cases. In Fig. 1(a), the free-energy curve has minima offset from zero magnetic moment. It is therefore energetically favorable for the system to possess a "well-defined" nonzero magnetic moment. The symmetric double minimum indicates that parallel (positive) and antiparallel (negative) orientations are equally probable. A magnetic phase described by Fig. 1(a) would consist of well-defined but totally randomized atomic magnetic moments. In Fig. 1(b), the minimum of free energy occurs at a magnetic-moment amplitude of zero. In the absence of spin fluctuations, such an atom would have zero local spin density. However, instantaneous moments could theoretically appear via the thermal population of fluctuations in both spin amplitude and direction. Magnetic systems whose atoms are described by Fig. 1(a) are often called "strong" magnets; systems described by Fig. 1(b) are often called "weak" magnets. Above T_N, chromium has been consistently theoretically described[11–15] by Fig. 1(b).

Experimentally, the existence (or nonexistence) of well-defined magnetic moments above T_N is unclear. Early neutron-diffraction experiments[5] on Cr concluded that localized atomic magnetic moments do not exist above T_N. However, more recent neutron-diffraction studies[2,3] reveal the persistence of unusual magnetic phenomena well above T_N. Elastic magnetic scattering indicative of a remnant commensurate AF order has been observed as high as 140 K above T_N. Well-defined spin-wave excitations have also been observed throughout the AF- to PM-phase transition. New estimates[2] for the effective atomic moment above T_N are $0.16 \mu_B$ at 500 K; nonzero, but considerably reduced from the $0.43 \mu_B$ rms
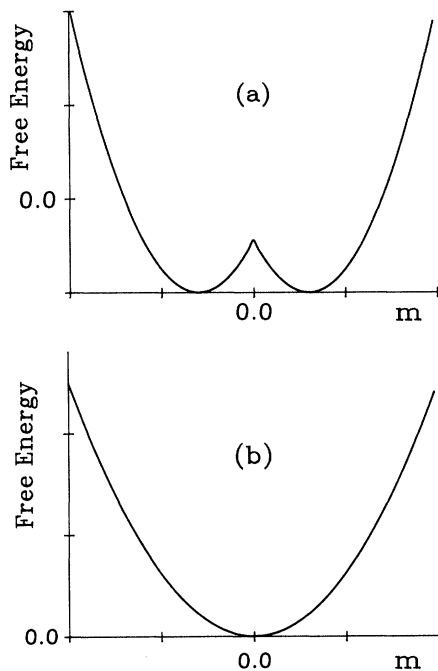
FIG. 1. Free energy plotted against the magnitude of the atomic (local) magnetic moment m for the paramagnetic phase of a magnetic metal. In (a) the nonzero minima indicate that well-defined local magnetic moments exist theoretically. In (b) the minimum of the free energy occurs at a magnetic-moment magnitude of zero, indicating that well-defined atomic magnetic moments do not exist theoretically.
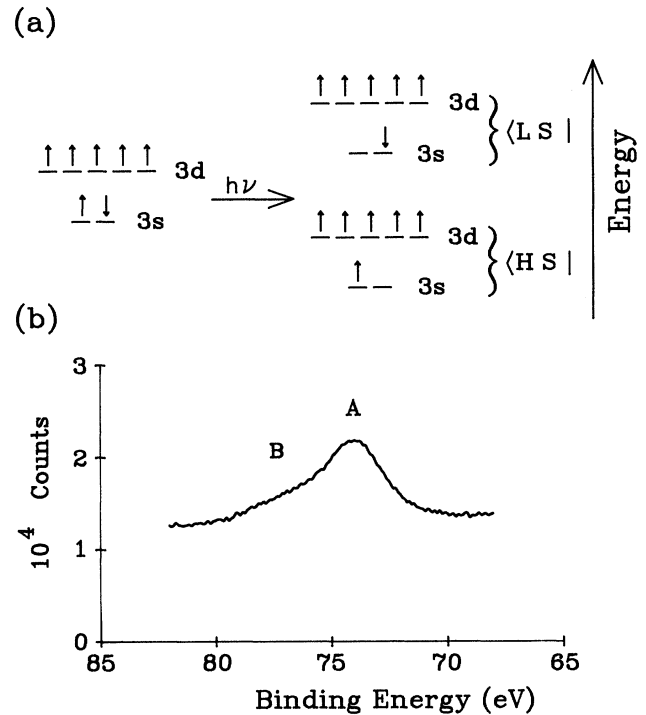

FIG. 2. (a) One-electron depiction of the intra-atomic exchange model as it applies to $3s$ photoemission from a Cr atom. (b) A Cr $3s$ spectrum ($h\nu = 1253.6$ eV, 1.2 eV energy resolution) collected from Cr(001) metal.

moment below T_N inferred from neutron diffraction.

Thermal-expansion measurements of Cr have also been examined for information on atomic magnetic moments. Two theoretical interpretations of the existing data come to conflicting conclusions regarding the existence of well-defined local moments above T_N. Analyzing the experimental data of Bolef and De Klerk,[16] Holden, Heine, and Samson[17] concluded that the rms Cr moment is reduced by only 3% in the transition to the PM phase. However, Kaiser and Haines,[18] interpreting the data of Roberts, White, and Fawcett[19] concluded that no well-defined local moments exist in the Cr above T_N.

X-ray photoelectron spectroscopy (XPS) is sensitive to the local atomic magnetic moment via core-level multiplet splitting.[20,21] Figure 2(a) presents the use of the intra-atomic exchange model in describing photoelectric excitation of a $3s$ electron in atomic Cr. Final-state intra-atomic exchange between the remaining $3s$ electron and the net valence $3d$ spin causes a splitting of the $3s$ XPS peaks into high-spin ($\langle \text{HS}|$) and low-spin ($\langle \text{LS}|$) components. One-electron theory[20−22] predicts the $3s$ multiplet splitting ΔE between $E(\langle \text{HS}|)$ and $E(\langle \text{LS}|)$ to be

$$\Delta E \equiv E(\langle \text{LS}|) - E(\langle \text{HS}|) = (2S+1)K(3s,3d) , \quad (2)$$

where S is the initial-state atomic spin and $K(3s,3d)$ is the exchange integral between $3s$ and $3d$ orbitals. Intra-shell electron correlation[23−25] can reduce the values of ΔE from the values predicted by Eq. (2). However, the

existence of the exchange-split line shape is directly caused by a net valence $3d$ spin and therefore the local atomic magnetic moment. The small spatial extent of the Cr $3s$ orbital[26] limits the $3s$-$3d$ exchange interaction to within 1 Å of the atomic center. Consequently the multiplet splitting is attributable to a very local spin density.

An experimental $3s$ XPS spectrum measured from Cr(001) is shown in Fig. 2(b). The solid-state line shape consists of a large component (referred to hereafter as component A) with binding energy 74.1 eV, and a smaller shoulder (referred to hereafter as component B) on the high-binding-energy side of component A. Since Cr metal is thought to possess a distribution of magnetic moments [Eq. (1)], the observed metallic $3s$ line shape is most likely a composite of many exchange-split $3s$ doublets as suggested by Fig. 2(a). This motivates our use of the term "components" rather than "peaks" for the spectral features A and B. Component A may in an average way be associated with the $\langle \text{HS}|$ final state; component B would have mostly $\langle \text{LS}|$ character. The validity of Fig. 2(a) in describing $3s$ XPS line shapes in magnetic metals will be discussed.

This paper presents a temperature-dependent XPS study of the Cr $3s$ level of Cr metal over a wide temperature range spanning T_N. The experimental details are given in Sec. II. The spectral results are presented in Sec. III and are discussed in Sec. IV. The relationship of this work to previous XPS measurements is described in Sec. V. Finally, the main conclusions are summarized in Sec. VI.

II. EXPERIMENT

The experimental arrangement will be described in some detail. All measurements were made in an ultrahigh-vacuum chamber constructed of μ metal. The chamber is evacuated with ion pumps and a Ti sublimation pump to a base pressure of 6×10^{-11} Torr. Typical operating pressures are 3×10^{-10} Torr. XPS is excited with a high-power Mg $K\alpha$ ($h\nu = 1253.6$ eV, unmonochromatized) x-ray source designed to operate continuously at 800 W. Typical operating powers were 300–510 W. Photoelectrons are analyzed with a V. G. ESCALAB MkII 150° spherical sector, 150-mm-mean-radius electron-energy analyzer with a variable entrance aperture. These measurements employed a 5° full angle of acceptance. Low-energy electron-diffraction (LEED) observations were used to monitor surface crystallographic order.

The sample mount consisted of an electron-bombardment heater in which a W filament is floated to high negative potential with respect to the grounded sample. This allowed high-temperature XPS studies. Low-temperature data were acquired using liquid-nitrogen cooling. Temperatures were measured using a Chromel-Alumel thermocouple spot welded near the sample, and are accurate to within 20°.

The sample was a high-purity Cr(001) single crystal that had been used in previous studies.[8,27–29] For those studies, the sample had been spark cut to within $\pm 0.5°$ of the (001) plane and mechanically polished (0.5 μm diamond paste) to a mirror finish. Extensive argon-ion bombardment with high-temperature annealing produced a surface and near-surface region free of nitrogen. For the present study, the crystal was cyclically argon-ion bombarded and annealed (1113 K) for a few days until the $p(1 \times 1)$ LEED pattern characteristic of the clean surface emerged. At this point, no impurities (C,O,N) were detectable by XPS. After 20–30 min in the vacuum, an oxygen $1s$ XPS peak started to grow in, and faint and broad $c(2 \times 2)$ LEED spots began to appear. This contamination was not alleviated by running liquid nitrogen through a cryoshroud surrounding the Ti sublimation pump. All spectra reported here were acquired on samples that had been exposed to the vacuum for less than 20 min. In between XPS runs, the crystal was sputtered for ~ 20 min to remove impurities and then annealed to 1113 K. Occasionally the sample was flashed to 1113 K to remove absorbed contaminants.

For all spectra, the sample was oriented so that the electron analyzer accepted electrons along the surface normal. Some measurements were made on a $c(2 \times 2)$N/Cr(001) surface. These samples were prepared by exposing a clean Cr(001) surface at $T = 573$ K to 10 L (1 langmuir $= 1$ L $\equiv 1 \times 10^{-6}$ Torr sec) of high-purity (99.99%) nitrogen gas.

III. RESULTS

Figures 3 and 4 present Cr $3s$ XPS spectra recorded at a variety of temperatures using an instrumental energy resolution of 1.7 eV full width at half maximum (FWHM). The dotted spectra are taken at the tempera-
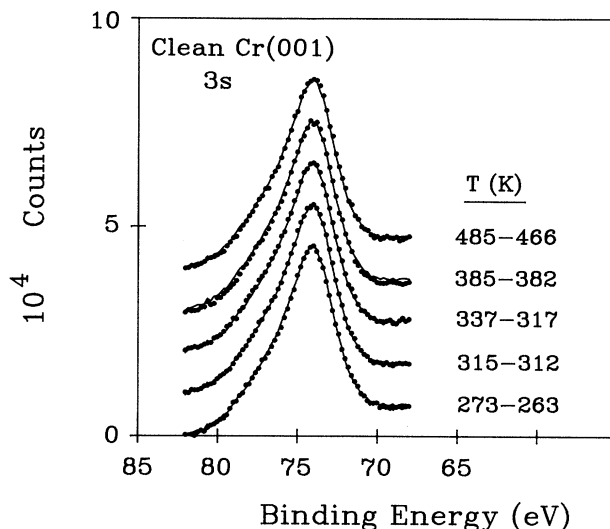

FIG. 3. Comparison of Cr $3s$ XPS spectra measured from clean Cr(001) at various temperatures. The solid line in each comparison is the Cr $3s$ XPS spectrum measured for temperatures (176–215 K) well below T_N (311 K). The dots denote the spectrum acquired at the temperatures listed. The instrumental energy resolution is 1.7 eV FWHM.

tures indicated in the figures. The solid lines show a Cr $3s$ XPS spectrum recorded at temperatures (176–215 K) well below T_N (311 K). For these comparisons, the spectra have had a constant background subtracted, have been normalized at component A, and have been rigidly shifted in intensity to clarify the presentation. Figures 3 and 4 reveal that the Cr $3s$ XPS line shape does not change as the temperature is raised up to and well beyond T_N. An analogous study using an improved energy resolution of 1.2 eV FWHM (but having a poorer statistical
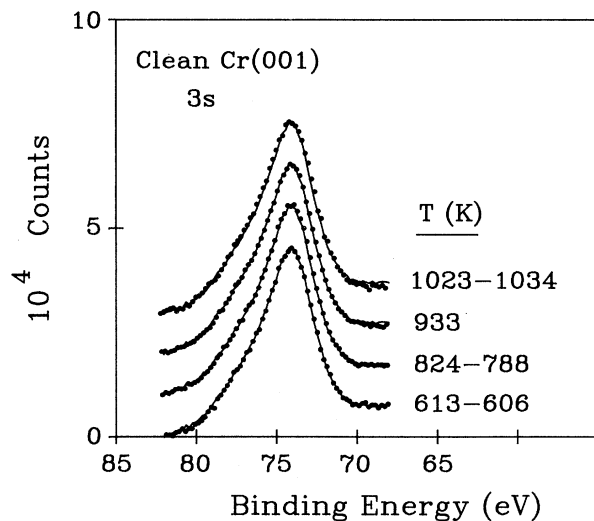

FIG. 4. Comparison of Cr $3s$ XPS spectra measured from clean Cr(001) at various temperatures. The solid line in each comparison is the Cr $3s$ XPS spectrum measured for temperatures (176–215 K) well below T_N (311 K). The dots denote the spectrum acquired at the temperatures listed. The instrumental resolution is 1.7 eV FWHM.
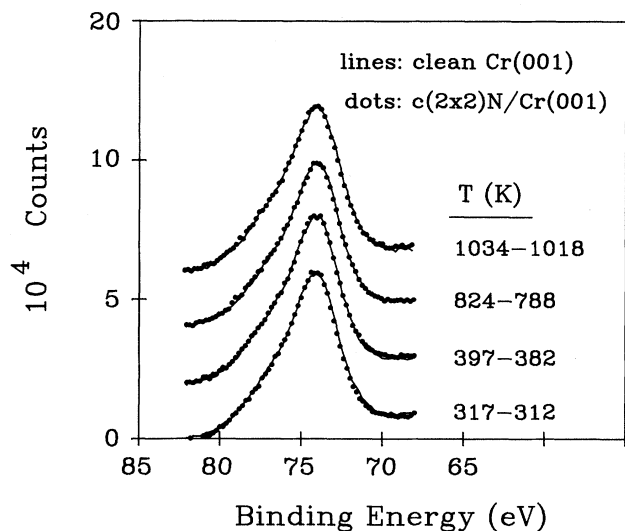
FIG. 5. Comparison of clean Cr(001) $3s$ XPS spectra (lines) with those of $c(2\times2)$N/Cr(001) (dots), at various temperatures. The instrumental energy resolution is 1.7 eV FWHM.

level in the data) yielded the same result: no evidence was found for a temperature-induced variation of the Cr $3s$ XPS line shape.

Figure 5 shows that this result is independent of surface contaminants, or surface adsorption. Figure 5 compares $3s$ XPS spectra from clean Cr(001) with those from $c(2\times2)$N/Cr(001), using the same background subtraction and normalization procedures as for Figs. 3 and 4. The Cr $3s$ line shape itself, as well as its insensitivity to temperature, are independent of the presence of 0.5 monolayer of an atomic adsorbate on the surface. XPS and LEED measurements were made to determine that the structure and coverage of the nitrogen adlayer were unaffected over the temperature range of Fig. 5. It was also observed that the $3s$ *line shape* was unaffected by changes in the polar angle of electron detection. Thus, while electron diffraction could change the overall intensity of the $3s$ envelope and its signal-to-background ratio, the relative intensities of the two components A and B remained unaltered.

IV. DISCUSSION

The results of Sec. III indicate that the local $3d$ spin density within 1 Å of the Cr atomic center is independent of temperature up to $3.3T_N$. This conclusion is based on the validity of the intra-atomic exchange model Fig. 2(a) in explaining the $3s$ XPS line shapes of magnetic atoms and ions. One could argue that the Cr $3s$ line shape is independent of temperature because this line shape is not determined by initial-state magnetism but by final-state phenomena that are unrelated to magnetism. Reference 29 provides arguments for why such phenomena cannot consistently explain Cr $3s$ photoemission data. Recently, very strong evidence has been presented in favor of the intra-atomic exchange model of the $3s$ line shapes. Hermsmeier *et al.*[30] have compared the Mn $3s$ photo-

emission line shape from gas-phase atomic Mn with the corresponding spectra of Mn^{2+} from MnO and MnF_2. The atomic and solid-state $3s$ spectra are quite similar, indicating that the solid-state environment does not significantly alter the $3s$ line shape. This argues convincingly for an intra-atomic exchange interpretation of the Mn $3s$ line shape, and of the Cr $3s$ line shape as well (Fig. 2). It has also been argued that for $3d$ transition-metal systems with fewer than six $3d$ electrons, the final state has the same $3d$-electron count as the initial state.[31]

A quite explicit demonstration of the intra-atomic exchange splitting of the Fe $3s$ XPS peak has been recently reported.[32,33] In this work,[32,33] the spin polarization of the Fe $3s$ peaks, a property unique to the intra-atomic-exchange view, was detected. The photoelectrons producing the $\langle LS|$ component were found to have majority-spin polarization; the photoelectrons leading to the $\langle HS|$ final state were found to have a minority-spin polarization, in excellent accord with the multiplet-splitting model of Fig. 2(a).

Further evidence that the Cr $3s$ XPS line shape is determined by intra-atomic exchange is provided by the observed variation of the $3s$ line shape at the Cr(001) surface,[29] and in thin films of Cr deposited on Ag(001).[34] These variations are most consistently attributed to variations in the Cr atomic spin S. Thus the temperature independence of the Cr $3s$ XPS line shape reported here indicates that the $3d$ spin density within 1 Å of the Cr atomic center is not changing for temperatures up to 715 K above T_N.

Internal strain is known to cause an increase of the bulk Cr T_N up to ~600 K.[1] It is highly unlikely that stress is causing the phenomenon observed here. Our Cr(001) sample has been annealed hundreds of times over its lifetime, and any internal stress would have long since been annealed out.

It is important to establish the extent to which these Cr $3s$ XPS measurements reflect bulk Cr. The kinetic energy of the Cr $3s$ photoelectrons in this study is ~1175 eV. Based on inelastic–mean-free-path calculations,[35] we estimate that the first ~14 layers of Cr contribute substantially to the $3s$ line shape. For most metals and most physical properties, bulklike behavior is observed by the third or fourth layer. Thus the comparison of XPS results with results from "bulk" techniques is ordinarily straightforward. This is not *a priori* the case for Cr(001).

Recent experimental[8,27−29] and theoretical work[11,14,28,36−41] has suggested the existence of a ferromagnetic surface layer on an otherwise AF Cr(001) crystal. In the case of Cr(001) the word ferromagnetic is meant to convey that the surface atoms posses unusually large magnetic moments that couple ferromagnetically to each other with a strength and thermal stability unique to the surface plane. However, photoemission experiments[8] of Cr(001) have indicated that the second-layer magnetization points opposite to the surface-layer magnetization, thereby forming a near-surface Cr(001) AF order. Thus, in the presence of monatomic steps, the surface consists of terraces. Within each terrace, the surface moments would couple ferromagnetically in the sense above, thereby establishing a unique ferromagnetic terrace electronic

structure. However, neighboring terraces would, by virtue of the near-surface AF order, have their magnetizations pointed oppositely. This "topological" AF surface order is fully consistent with the photoemission measurements,[8,27-29] has been proposed and examined theoretically,[42] and has been recently detected experimentally.[43]

The relevance of this surface phenomenon to the present study is the magnitude of the surface magnetic disturbance and its considerable theoretical penetration into the subsurface layers. A theoretical magnetization profile[41] at $T = 0$ K for Cr(001) is shown in Fig. 6 and is typical of most recent predictions[11,14,37,40] for Cr(001) surface magnetism. In this figure, the diameter of an atom is drawn proportional to its predicted spin polarization. Even five layers into the crystal, the spin polarization is predicted to be 0.86 electron, still larger than the maximum bulk value of ~ 0.6 electron. It would appear that Cr(001) is a poor choice to study bulk Cr electronic and magnetic properties. But it is not clear that using a polycrystalline Cr sample would reduce this problem, for the surface magnetic enhancement likely exists on all Cr surfaces. Cr(001) was chosen for this study because its surface[27-29] and near-surface[8] properties have been extensively characterized.

Our Cr 3s XPS measurements encompass the region of enhanced magnetization portrayed in Fig. 6 as well as the next nine layers below. If surface phenomena were causing the temperature insensitivity of the Cr 3s XPS line shape, then one would expect the results of the temperature-dependent study to be sensitive to surface
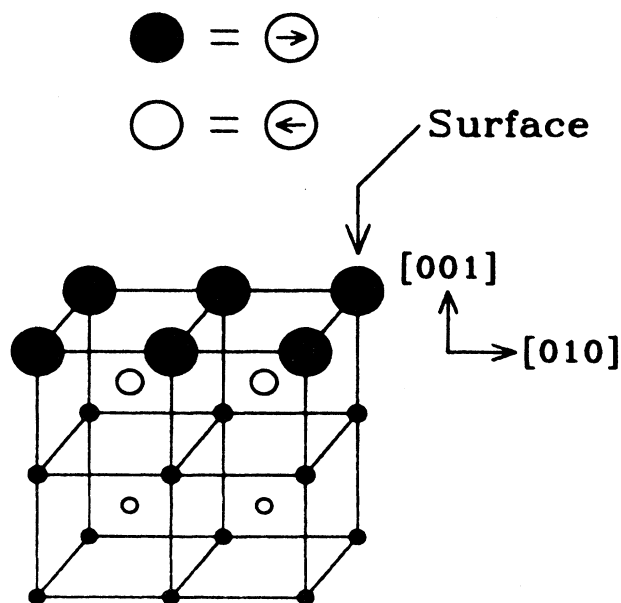

FIG. 6. The theoretical prediction for Cr(001) surface and near-surface magnetism. Atoms whose magnetic moments point to the right are indicated by darkened spheres. Atoms whose magnetic moments point to the left are symbolized by open spheres. The diameter of a sphere representing an atom is drawn proportional to the magnitude of the atom's spin polarization, as predicted in Ref. 41. The surface spin polarization is predicted to be 3.00 electrons.

adsorption. Indeed the Cr 3s photoemission line shape, observed under conditions of extreme surface sensitivity, shows a sharp sensitivity to 0.5 monolayer contamination.[29] Surface states characteristic of the ferromagnetic surface layer are also highly surface sensitive.[27,28] Figure 5 compares Cr 3s XPS spectra obtained for a clean Cr(001) surface and a Cr(001) surface contaminated with a half monolayer of nitrogen. No variation in the 3s line shape or its temperature dependence is observed. In addition, the Cr 3s XPS line shape is unaffected by surface disorder produced by argon-ion bombardment and confirmed by LEED. We conclude that the surface contribution to the present measurements is very minor. But it seems unlikely that the XPS results are perfectly representative of bulk Cr. It is more likely that they are representative of an AF Cr region with a slightly enhanced average magnetization.

The thermal insensitivity of the Cr 3s XPS multiplet-split line shape is theoretically surprising irrespective of the location of the photoemitting atom. The lastest spin-fluctuation calculations[11] for bulk chromium predict a 40% reduction of the amplitude of the local magnetic moment as the temperature is raised from 0 K to T_N. Above T_N, the magnetic moment amplitude is predicted to increase as spin fluctuations are thermally populated. No self-consistent moment is thought to exist[11-15] for bulk Cr above T_N, as depicted in Fig. 1(b). For the surface, spin-fluctuation calculations[11,14] predict a 10% (Ref. 14) to 30% (Ref. 11) decrease in the mean-square moment at the surface Curie temperature, followed by a steady increase in the moment magnitude as surface spin fluctuations are populated. A surface magnetic phase transition temperature of 780 K was found experimentally.[27] Theoretically, the surface magnetic moment above the surface transition temperature is thought to be more well defined locally,[11,14] as in Fig. 1(a).

Our observation that the 3d spin density within 1 Å of the Cr atomic center is independent of temperature is inconsistent with these theories in two regards. First we find no evidence for a decrease in local atomic magnetic moment (local spin density) as the temperature is raised up to T_N. A decreased atomic moment would be expected to produce a narrowing of the overall 3s XPS line shape, as predicted by Eq. (1) and observed in XPS studies of Cr compounds.[44] No such narrowing is observed. Second, we find no evidence of a steadily increasing mean-square moment (indicative of spin fluctuations) as the temperature is raised far above the magnetic phase transition temperature. Such an increase would produce a broadening of the 3s multiplet profile at high temperatures, which is not observed. Note that in Fig. 4, the maximum temperature measured is ~ 715 K above T_N and ~ 246 K above the experimentally determined[27] surface magnetic-phase-transition temperature.

The observed invariance of the 3s multiplet splitting is also surprising, given the ARPES observations. The loss of AF order in Cr has been directly observed by ARPES, both in the "bulk" of Cr(110) (Refs. 9 and 10) and in the very-near-surface region[8] of Cr(001). What is the length scale of these ARPES observations? ARPES studies of valence-band dispersion in thin films[45] suggest that a full

three-dimensional itinerant-electronic structure requires ~ 5 atomic layers to develop. We speculate that the same length scale probably applies to magnetism. Thus a disappearance of the influence of AF order on the itinerant-electronic structure observed in ARPES signals the loss of AF order within the range of ~ 5 layers or equivalently ~ 6 Å in Cr.[46] *The present 3s XPS measurements therefore reveal a persistent local magnetic moment in the experimentally observed absence of short-range itinerant-electron spin order in the range of* ~ 6 Å. Many theories of itinerant-electron magnetism predict[17,47−51] that as neighboring moments tilt away from each other (i.e., as short-range magnetic order is destroyed), the magnitude of local magnetic moments decreases. Our measurements indicate that, at least in Cr, a loss of magnetic order need not reduce the local spin density seen in XPS.

It is interesting to note that ARPES measurements of valence bands can directly reveal thermal reductions in exchange splittings as temperature-induced energy shifts of exchange-split valence states. For instance, this has been clearly observed in Ni, using spin-resolved[52] and spin-integrated[53] ARPES, as well as for a surface state on Cr(001).[27] Yet for Cr we find no evidence for a thermal variation of the $3s$-$3d$ exchange splitting. Since the time scales of ARPES and core-level XPS are the same, one cannot conclude that the time scale of the XPS measurement is in some way incompatible with the observation of a magnetic phase transition.

Our broad interpretation of the Cr $3s$ XPS results attempts to reconcile a decrease in the atomic magnetic moment with the Cr $3s$ XPS data. Figure 7 plots the radial distribution functions $[r^2 R_{nl}^2(r)]$ (Ref. 26) versus ra-
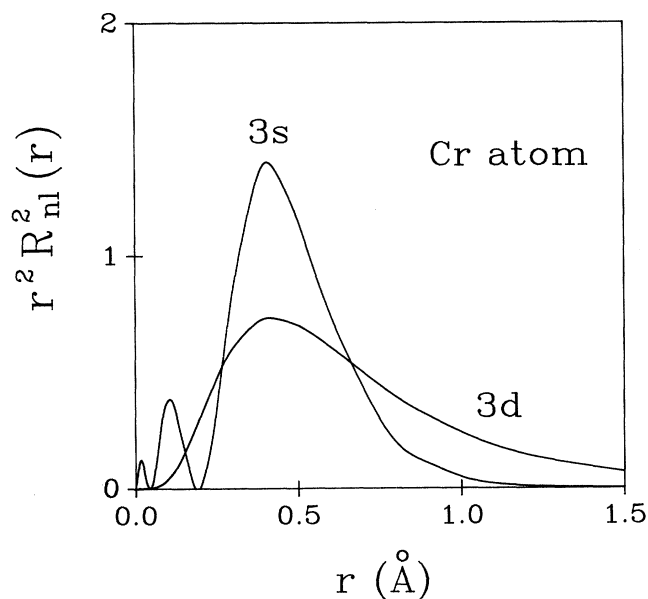

FIG. 7. The radial distribution function $r^2 R_{nl}^2(r)$ plotted against radial distance r for the $3s$ and $3d$ levels of atomic Cr. The figure is created from the calculations of Ref. 26. $R_{nl}(r)$ are the normalized nonrelativistic self-consistent Hartree-Fock-Slater radial wave functions.

dius r for the $3s$ and $3d$ levels of atomic Cr. The small spatial extent of the $3s$ orbital limits the $3s$-$3d$ exchange interaction to regions within 1 Å of the atomic center. Consequently, the multiplet splitting ΔE is attributable to a very local spin density, and is insensitive to changes in the solid-state environment at the periphery ($r > 1$ Å) of the photoemitting atom. This view is consistent with the observed linearity of ΔE with $2S + 1$ in Mn compounds.[54] The Mn $3s$ multiplet splitting is altered by changes in the atomic spin caused by an increased oxidation state because oxidation produces a strong local change in the spin density. However, the Mn $3s$ multiplet-split line shape is relatively unaffected by the peripheral differences in the crystalline environment present in these Mn compounds.[54]

Given this local nature of the $3s$ multiplet splitting, the Cr $3s$ XPS results suggest that even for this itinerant-electron system in which there is clear evidence for a disruption of AF order in the bulk,[9,10] as well as in the near Cr(001) surface region,[8] the local spin density within 1 Å of a Cr atom is the same in the AF and PM phases. We speculate that *if temperature-induced changes in the 3d spin polarization occur in Cr, then these variations occur at the periphery of the metallic atom, i.e., outside a radius of 1 Å, leaving the spin density within* ~ 1 Å *unaffected.* This postulate would explain why valence-band ARPES detects the thermal disruption of AF order in Cr, but the $3s$ XPS core-level measurement is unaffected. A direct ARPES measurement of a $3d$ valence-band state samples the $3d$ orbitals in their entirety. Valence-band ARPES studies are thus sensitive to peripheral and itinerant influences on the $3d$ valence band. One such itinerant influence is the effect of AF order on the periodicity of valence-band dispersions. It is the sensitivity of valence-band dispersion periodicity to real-space periodicity (a peripheral effect) that makes ARPES sensitive to the AF order.[8] Thus, if thermally induced reductions in the magnetic moment take place at the periphery of the magnetic $3d$ atom, valence-band ARPES would detect this, as is clearly observed for Ni (Refs. 50 and 51) and for a Cr(001) surface state.[27] However, the $3s$ XPS measurement, being highly local, would not reflect $3d$ spin-density variations confined to the periphery of the atom. Note from Fig. 7 that a substantial portion of the $3d$ radial distribution function extends beyond a radius of 1 Å. This suggests that peripheral effects could play a substantial role in shaping high-temperature magnetic phenomena.

This scenario would also explain apparent conflicts with neutron-diffraction data that suggest a sizable reduction of the magnetic moment from $\sim 0.43 \mu_B$ in the AF phase to $\sim 0.16 \mu_B$ at 500 K. Neutron diffraction is sensitive to magnetism throughout a crystal. The effective atomic moment is calculated[2] by averaging the magnetization over a theoretical atomic volume ($a^3/2$ in the case of Cr). A loss of spin polarization at the atomic periphery ($r > 1$ Å) would clearly affect neutron diffraction. The residual effective moment seen in neutron diffraction above T_{N_0} may then be the residual local spin density within 1 Å of the Cr atom, i.e., the spin density relevant to the Cr $3s$ XPS measurements. The time scale

difference between neutron diffraction (10^{-12} sec) and XPS (10^{-15} sec) is often invoked to explain discrepancies between the two techniques. In the scenario above, it is the length-scale difference between the two techniques that is of most concern.

Note that Ref. 29 reports variations of the Cr $3s$ line shape at the Cr(001) surface that are generally consistent with an enhanced Cr(001) surface magnetization. This would indicate that large increases in magnetization caused by the loss of nearest neighbors at the Cr(001) surface produce local ($r < 1$ Å) variations in the $3d$ spin density.

V. RELATIONSHIP TO PREVIOUS WORK

The experiments presented here are particularly related to two previous $3s$ XPS measurements. The Fe $3s$ XPS line shape has been studied[55] below T_C and at 1.04 T_C. No evidence for a line-shape change was observed. In retrospect, this result is not surprising. There now exists a theoretical[12,15,47−49,56] and experimental[17,57,58] consensus that paramagnetic iron is described by Fig. 1(a), i.e., that well-defined magnetic moments exist above T_C with perhaps only a small ($\sim 10\%$) decrease in the magnitude of the atomic magnetic moment from its ferromagnetic value.

An investigation[54] has also been made of the $3s$ XPS line shape of metallic Mn in the paramagnetic phase. Although a temperature-dependent study through T_N was not made, a single measurement in the PM phase revealed a Mn $3s$ splitting indicative of a magnetic moment of $2.5\mu_B$. Again, in retrospect, this result is also expected. Theoretically,[13,15] Mn is a borderline "disordered local moment" metal. The PM phase of δ (bcc) Mn is thought[15] to be described by Fig. 1(a) with large ($\sim 2\mu_B$) local magnetic moments. The PM phase of γ (fcc) Mn has been theoretically described by Fig. 1(a) (Ref. 13) and Fig. 1(b).[15] Evidence for a sizable ($\sim 0.5\mu_B$) effective magnetic moment is also found in neutron-diffraction studies[59] of PM Mn. The observation of a Mn $3s$ splitting above T_N is therefore not surprising.

What distinguishes the present study from these prior measurements is (1) the Cr $3s$ XPS measurements extend well below T_N and far above T_N; (2) the measurements are made for Cr, a metal that by all theories should not have a well-defined magnetic moment at high temperatures in the bulk; and (3) the core-level study was conducted on a metal for which a disruption of a short-range magnetic order on the scale of ~ 6 Å has been clearly observed by ARPES.

VI. SUMMARY

A temperature-dependent study of the Cr $3s$ XPS line shape is reported. As the temperature is varied from well below T_N to far above it ($\sim 3.3 T_N$), no variation of the Cr $3s$ line shape is observed. This invariance is insensitive to surface chemisorption, suggesting that the behavior is not caused by the enhanced Cr(001) surface magnetism. The results indicate that the atomic $3d$ spin density within ~ 1 Å of the atomic center is the same in the AF and PM phases of Cr. No evidence is found for a theoretically predicted collapse of the atomic magnetic moment in Cr, or for the thermal population of spin fluctuations. The results are particularly striking, given the direct ARPES observation of the loss of AF order in Cr. The results are therefore a demonstration of the persistence of local atomic spin density in the absence of short-range magnetic order on the scale of ~ 6 Å.

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[1]E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).

[2]B. H. Grier, G. Shirane, and S. A. Werner, Phys. Rev. B **31**, 2892 (1985).

[3]C. R. Fincher, Jr., G. Shirane, and S. A. Werner, Phys. Rev. B **24**, 1312 (1981).

[4]S. K. Burke, W. G. Stirling, K. R. A. Ziebeck, and J. G. Booth, Phys. Rev. Lett. **51**, 494 (1983).

[5]M. K. Wilkinson, E. O. Wollan, W. C. Koehler, and J. W. Cable, Phys. Rev. **127**, 2080 (1962).

[6]A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).

[7]J. E. Hirsch, Phys. Rev. B **41**, 6828 (1990).

[8]L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **31**, 6379 (1985).

[9]Y. Sakisaka, T. Komeda, M. Onchi, H. Kato, S. Suzuki, E. Edamoto, and Y. Aiura, Phys. Rev. B **38**, 1131 (1988).

[10]L. I. Johansson, L. -G. Petersson, K. -F. Berggren, and J. W. Allen, Phys. Rev. B **22**, 3294 (1980).

[11]H. Hasegawa, J. Phys. F **16**, 1555 (1986).

[12]A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F **13**, 979 (1983).

[13]S. N. Evangelou, H. Hasegawa, and D. M. Edwards, J. Phys. F **12**, 2035 (1982).

[14]D. R. Grempel, Phys. Rev. B **24**, 3928 (1981).

[15]V. Heine, J. H. Samson, and C. M. M. Nex, J. Phys. F **11**, 2645 (1981).

[16]D. I. Bolef and J. De Klerk, Phys. Rev. **129**, 1063 (1963).

[17]A. J. Holden, V. Heine, and J. H. Samson, J. Phys. F **14**, 1005 (1984).

[18]A. B. Kaiser and E. M. Haines, J. Phys. F **15**, 1765 (1985).

[19]R. B. Roberts, G. K. White, and E. Fawcett, Physica B **119**, 63 (1983).

[20]D. A. Shirley, in *Photoemission in Solids I,* edited by M. Cardona and L. Ley, Topics in Applied Physics (Springer-Verlag, Berlin, 1978), p. 165.

[21]C. S. Fadley, in *Electron Spectroscopy,* edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 781.

[22]J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

[23]P. A. Cox, J. Electron Spectrosc. Relat. Phenom. **22**, 77 (1981).

[24]J. R. Leite, J. C. Rodrigues, A. C. Ferraz, and A. C. Pavao, Phys. Rev. B **16**, 978 (1977).

[25]P. S. Bagus, A. J. Freeman, and F. Sasaki, Phys. Rev. Lett. **30**, 850 (1973).

[26]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

[27]L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **30**, 1048 (1984).

[28]L. E. Klebanoff, R. H. Victora, L. M. Falicov, and D. A. Shirley, Phys. Rev. B **32**, 1997 (1985).

[29]L. E. Klebanoff and D. A. Shirley, Phys. Rev. B **33**, 5301 (1986).

[30]B. Hermsmeier, C. S. Fadley, M. O. Krause, J. Jimenez-Mier, P. Gerard, and S. T. Manson, Phys. Rev. Lett. **61**, 2592 (1988).

[31]V. Kinsinger, I. Sander, P. Steiner, R. Zimmermann, and S. Hüfner, Solid State Commun. **73**, 527 (1990).

[32]C. Carbone, T. Kachel, R. Rochow, and W. Gudat, Z. Phys. B **79**, 325 (1990).

[33]F. U. Hillebrecht, R. Jungblot, and E. Kisker, Phys. Rev. Lett. **65**, 2450 (1990).

[34]D. A. Newstead, C. Norris, C. Binns, and P. C. Stephenson, J. Phys. C **20**, 6245 (1987).

[35]S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **11**, 577 (1988).

[36]Y. Teraoka and J. Kanamori, in *Transition Metals,* edited by M. J. G. Lee, IOP Conf. Proc. No. 39 (Institute of Physics and Physical Society, London, 1978), p. 588.

[37]G. Allan, Surf. Sci. **74**, 79 (1978).

[38]G. Allan, Phys. Rev. B **19**, 4774 (1979).

[39]G. Allan, Surf. Sci. Rep. **1**, 121 (1981).

[40]C. L. Fu and A. J. Freeman, Phys. Rev. B **33**, 1755 (1986).

[41]R. H. Victora and L. M. Falicov, Phys. Rev. B **31**, 7335 (1985).

[42]S. Blügel, D. Pescia, and P. H. Dederichs, Phys. Rev. B **39**, 1392 (1989).

[43]R. Wiesendanger, H. -J. Güntherodt, G. Güntherodt, R. J. Gambina, and R. Ruf, Phys. Rev. Lett. **65**, 247 (1990).

[44]D. T. Clark and D. B. Adams, Chem. Phys. Lett. **10**, 121 (1971).

[45]J. G. Tobin, S. W. Robey, L. E. Klebanoff, and D. A. Shirley, Phys. Rev. B **35**, 9056 (1987).

[46]A previous interpretation (Ref. 8) of the silver thin-film data of Ref. 45 concluded that the ARPES length scale was ~ 15 Å. This length was arrived at because five silver (111) layers have a thickness of ~ 15 Å. The revised distance of 6 Å reflects the view that it is the number of layers, and not the distance, that determines the evolution of three-dimensional valence-band behavior.

[47]M. V. You and V. Heine, J. Phys. F **12**, 177 (1982).

[48]A. J. Holden and M. V. You, J. Phys. **12**, 195 (1982).

[49]V. Korenman, J. L. Murray, and R. E. Prange, Phys. Rev. B **16**, 4032 (1977).

[50]V. Korenman, J. L. Murray, and R. E. Prange, Phys. Rev. B **16**, 4048 (1977).

[51]H. Capellmann, J. Phys. F **4**, 1466 (1974).

[52]H. Hopster, R. Raue, G. Guntherodt, E. Kisker, R Clauberg, and M. Campagna, Phys. Rev. Lett. **51**, 829 (1983).

[53]D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. **40**, 1514 (1978).

[54]F. R. McFeely, S. P. Kowalczyk, L. Ley, and D. A. Shirley, Solid State Commun. **15**, 1051 (1974).

[55]C. S. Fadley and D. A. Shirley, Phys. Rev. A **2**, 1109 (1970).

[56]J. Hubbard, Phys. Rev. B **19**, 2626 (1979).

[57]E. Kisker, K. Schröder, M. Campagna, and W. Gudat, Phys. Rev. Lett. **52**, 2285 (1984).

[58]J. W. Lynn, Phys. Rev. B **11**, 2624 (1975).

[59]C. G. Shull and M. K. Wilkinson, Rev. Mod. Phys. **25**, 100 (1953).