Temperature-dependent study of 3*s* multiplet splitting in ferromagnetic Ni

J. C. Glueckstein and L. E. Klebanoff
Department of Chemistry and Zettlemoyer Center for Surface Studies, Lehigh University, Bethlehem, Pennsylvania 18015, USA
(Received 26 June 2002; published 28 August 2003)

A high-resolution x-ray photoelectron spectroscopy (HRXPS) study of the Ni 3*s* core level is presented. Ni 3*s* HRXPS spectra were compared at $T=298$ K ($T=0.47T_c$) and 863 K ($T=1.37T_c$). No significant variation with temperature is observed. These HRXPS results, combined with prior spin-resolved x-ray photoelectron spectroscopy studies of Ni core levels, indicate the persistence of atomic magnetism in the paramagnetic phase of Ni on the length scale of ~0.75 Å. The data suggest that temperature-induced changes in the Ni 3*d* spin polarization occur at the periphery of the metallic atom, i.e., outside a radius of 0.75 Å, leaving the spin density within 0.75 Å unaffected.

DOI: 10.1103/PhysRevB.68.052407 PACS number(s): 71.70.Gm, 75.50.Cc, 79.60.−i

I. INTRODUCTION

Photoemission from ferromagnetic Ni has been an intensively studied subject, experimentally[1–4] and theoretically,[4–7] for almost 30 years. Both valence-hole and core-hole creation in Ni probe a variety of electronic phenomena including extra-atomic relaxation and core-level binding energy shifts,[4,5] electron correlation and exchange in narrow-band systems,[6,7] and spin polarization in Auger decay.[8]

Of particular interest has been the temperature dependence of the magnetic phenomena in Ni as revealed by spin-integrated and spin-resolved photoelectron spectroscopy and inverse photoelectron spectroscopy. Eastman *et al.*[9] used valence-band photoemission to reveal a reduction in the Ni valence exchange splitting of ~40% with increasing temperature. Using spin- and angle-resolved photoemission, Hopster *et al.*[10] also observed a collapsing of exchange-split valence-band states with increasing temperature, suggesting a reduction in exchange splitting of order ~50%. A reduced exchange splitting at elevated temperature was observed in spin-resolved valence-band photoemission studies of Ni (111),[11] and a collapsing band behavior has also been seen in inverse photoemission of unoccupied Ni valence bands.[12] A collapsing-band behavior has been inferred from Fermi surface photoemission measurements of spin-split *sp* states in Ni, although a more complex behavior was observed for 3*d*-derived valence bands in other regions of *k* space.[13]

Concurrent with these experimental observations have been developments in the theoretical study of temperature-dependent Ni magnetism. Early Stoner-Wohlfarth mean-field theory[14] predicted a collapse of the exchange splitting and the disappearance of all magnetic order and local magnetic moments as the temperature approaches the bulk Curie temperature, $T_c=\sim 630$ K. Later, developments in local band theory[15] predicted the existence of short-range magnetic order above T_c and a temperature-independent exchange splitting on the length scale of ~20 Å. More recently, calculations involving an effective medium approach to the Hubbard model have been compared to both photoemission and inverse photoemission spectra of Ni.[16] No indication of a stationary (i.e., temperature-independent) exchange splitting could be found. Instead, exchange-split photoemission and inverse photoemission peaks merged together with temperature in both theory and experiment.

Interestingly, the photoemission observations of a temperature-dependent Ni exchange splitting are confined to ''direct'' (i.e., nonresonant) photoemission or inverse photoemission measurements of the Ni valence band. Kakizaki *et al.*[17] measured the Ni 6-eV valence-band satellite in resonance with the 3*p* threshold and found no temperature dependence on the satellite line shape. This observation led the authors to conclude the existence of a temperature-independent exchange splitting in local ferromagnetic bands of Ni at elevated temperature. Very recently, Sinkovic *et al.*[18] have examined the Ni 3*d* valence spin polarization at the Ni $2p_{3/2}$ threshold using electron spin analysis and circularly polarized soft x-ray radiation. Up to $1.04T_c$, there was no change in the dichroic valence spin polarization, suggesting that the magnitude of the local magnetic moment was independent of temperature up to $1.04T_c$. The apparent contradiction between nonresonant valence-band photoemission (displaying collapsing exchange splitting) and resonant photoemission (displaying temperature-independent exchange splitting) was not explored in these prior studies.

Our experiment probes the Ni valence spin polarization within the radial extent of the 3*s* core level by examining the temperature dependence of 3*s*-3*d* multiplet splitting in Ni over the temperature range from 298 K ($0.47T_c$) to 863 K ($1.37T_c$). In contrast to the previous photoemission measurements, the local Ni spin polarization is probed well above T_c. There have been no prior studies of the temperature dependence of core-level photoemission from Ni. One reason for this is that, for many years, it was believed Ni core-level photoemission was not influenced by multiplet splitting, since the valence configuration for Ni upon core-hole creation was thought to be the nonmagnetic $3d^{10}$ configuration.[1,19] These assignments suggested that the Ni core-level line shape would not a useful probe of Ni magnetism.

More recently, many-body 3*d* configuration interaction (CI) calculations[6,7] employing the Anderson impurity model and many-body calculations by Menchero[20] have suggested that the final-state valence configuration in Ni, while predominantly $3d^{10}$, can have admixture from the magnetic $3d^9$ configuration. Recent spin-resolved x-ray photoelectron

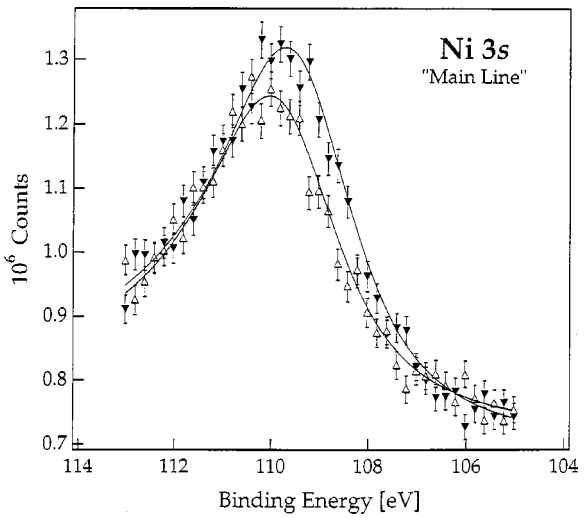

FIG. 1. Separate $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Ni 3*s* main component, for majority-spin (△) and minority-spin (▼) photoelectrons, respectively. The lines through the data are the result of an 11-point second-order Savitsky-Golay smooth through the raw $N\uparrow$ and $N\downarrow$ data points. Error bars are shown for both the $N\uparrow$ and $N\downarrow$ spectra. Data are reproduced from Ref. 3.

spectroscopy (SRXPS) studies[3,21] of the Ni 3*s* level show that the 3*s* photoemission peak is in fact dominated by 3*s*-3*d* intra-atomic exchange. The decomposition of the Ni 3*s* spectrum into ↑-spin and ↓-spin contributions is shown in Fig. 1 for the ''main'' Ni 3*s* component from 106–113 eV binding energy. The main Ni 3*s* peak shows a core-valence exchange splitting of 0.38 eV. If the Ni 3*d* spin polarization were to vanish within the radial extent of the Ni 3*s* orbital, the Ni 3*s* peak would narrow considerably. We examine below the line shape of the Ni 3*s* peak well below and well above the bulk Ni Curie temperature. The experimental details are described in Sec. II, with results presented and discussed in Sec. III. Conclusions are reviewed in Sec. IV.

II. EXPERIMENT

The high-energy-resolution XPS (HRXPS) measurements of Ni employed Lehigh University's SCIENTA ESCA-300 spectrometer, described elsewhere.[22] The overall instrumental energy resolution for these measurements was 0.36 eV full width at half maximum (FWHM) for the Ni 3*s* data. The pressure in the SCIENTA analysis chamber during measurement was $\sim 1\times 10^{-8}$ Torr for the 298 K measurements and $\sim 1\times 10^{-7}$ Torr for the high-temperature measurements. Surface cleanliness was checked repeatedly by XPS. Despite the modest vacuum conditions, XPS survey spectra before and after the measurements revealed only trace contamination of the Ni sample. Small amounts of surface contaminants would not affect the measurements, since the large (~1376 eV) kinetic energies and associated long (~19 Å) electron mean free path[23] of the outgoing 3*s* photoelectrons renders the HRXPS measurement an essentially bulk measurement.

The sample was a high-purity Ni foil, which was cleaned *in situ* by scraping with a tungsten carbide blade. A high-purity Cu foil, used for control measurements, was also cleaned by *in situ* scraping. The samples were heated *in situ* by resistive heating.

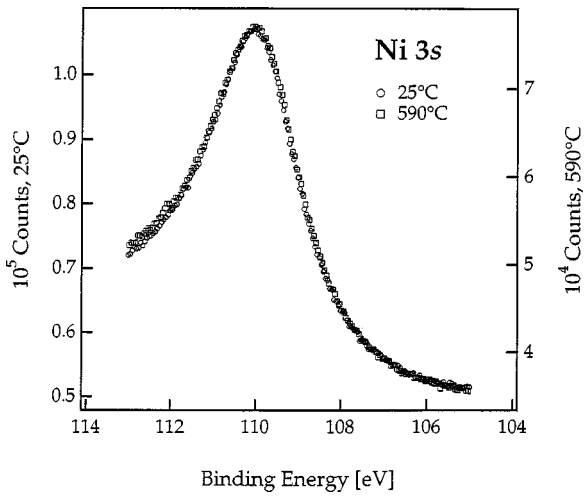

FIG. 2. HRXPS spectra of the Ni 3*s* level at 298 and 863 K.

III. RESULTS AND DISCUSSION

Figure 2 displays a HRXPS spectrum of the Ni 3*s* ''main'' component (from 106–113 eV binding energy) for temperatures well below (298 K) and well above (863 K) the bulk Ni Curie temperature of ~630 K. We find no significant variation in the Ni 3*s* line shape with temperature. Control HRXPS measurements on the Cu 3*s* level at 298 and 863 K also revealed no detectable line shape variation with temperature, which is expected since the 3*s* level of nonmagnetic Cu is not multiplet split. The Cu control measurement indicates that phonon-induced line width broadening does not contribute significantly to these HRXPS experiments, due to the large intrinsic energy widths of the 3*s* core peaks.

Comparison of the Cu 3*s* and Ni 3*s* photoemission line shapes allows an estimate of the sensitivity of the HRXPS measurement to changes in valence spin polarization. We take the Ni 3*s* FWHM to represent the exchange splitting due to 0.56 electrons (the bulk Ni valence spin polarization) and the Cu 3*s* FWHM to represent zero exchange splitting due to zero Cu valence spin polarization. From this assumption, we estimate a variation in the Ni 3*d* spin of ~0.07 electrons should be detectable as a reliably observable linewidth variation of 0.12 eV in the Ni 3*s* photoemission peak.

The temperature independence of the Ni 3*s* HRXPS spectra indicates that the 3*s*-3*d* exchange interaction, which determines the Ni 3*s* main component line shape (Fig. 1), does not change with temperature. The length scale of the persistent spin polarization can be estimated from the radial extent of the Ni 3*s* orbital. Figure 3 shows the radial distribution function $r^2R_{n1}^2(r)$ plotted against radial distance *r* for the 3*s* and 3*d* levels of atomic Ni. The calculation[24] is for the atomic configuration $4s^13d^9$, which is the expected configuration of Ni atoms in metallic Ni. The vast majority of the 3*s* probability density lies within 0.75 Å of the atomic center. Therefore, we conclude that the Ni 3*d* valence spin polariza-

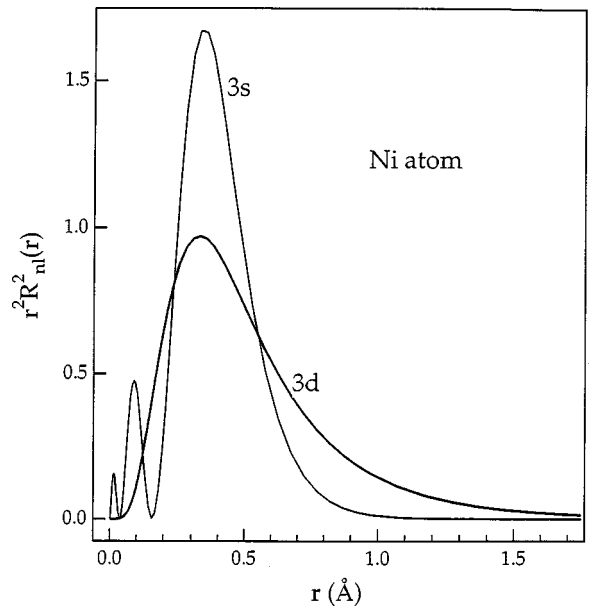

FIG. 3. Radial distribution function $r^2R_{nl}^2(r)$ plotted against radial distance r for the $3s$ and $3d$ levels of atomic Ni in the $4s^13d^9$ configuration. The figure is created from the calculations of Ref. 23. $R_{nl}(r)$ are the normalized nonrelativistic self-consistent Hartree-Fock Slater radial wave functions.

tion, within the ~0.75 Å radial extent of the $3s$ core level, does not vary up to $1.37T_c$, far into the paramagnetic phase of Ni.

Why does nonresonant valence-band measurement display collapsing band behavior, whereas valence-band photoemission in resonance with core excitation reveals a stationary (temperature-independent) exchange splitting? The HRXPS data suggest that the explanation lies with the persistent Ni $3d$ spin polarization within 0.75 Å of the atomic center. In the resonant photoemission experiments, the origin of the excitation is a highly localized $2p_{3/2}$ or $3p$ core level. Because the cross section for resonant valence-band photoemission necessarily involves valence-core overlap integrals, the resonant experiment is sensitive to the $3d$ spin polarization within the radial length scale of the photoemitting core level. This localization, induced in the resonant valence-band measurement, is significantly higher than the length scale associated with direct valence photoemission or inverse photoemission, which probe the entire radial extent of the $3d$ valence orbitals, on order of ~1.5 Å. Therefore, the resonant photoemission ''senses'' the atomic spin density within ~0.75 Å of the atomic center. The Ni HRXPS data indicate that this spin density does not vary even 233 K above T_c. Thus valence-band spectra measured at core-level absorption thresholds will not reveal temperature dependence in the valence-band behavior.

Although the intra-atomic ($r<0.75$ Å) spin density in Ni is temperature independent, the direct (nonresonant) photoemission and inverse photoemission studies of the Ni valence band still show a collapsing band behavior at elevated temperature. We speculate that if temperature-induced changes in the $3d$ spin polarization occur in Ni, then these variations occur at the periphery of the metallic atom, i.e., outside a radius of 0.75 Å, leaving the spin density within 0.75 Å unaffected. Since the direct photoemission and inverse photoemission techniques sample the Ni $3d$ band over its entire radial range, these spectroscopic techniques are sensitive to peripheral and itinerant influences on the $3d$ valence band. These peripheral influences are specifically responsible for interatomic magnetic phenomena in Ni, such as ferromagnetic order, valence-band dispersion, and valence-band exchange splitting. If a thermally induced reduction in the Ni valence spin polarization takes place at the periphery of the Ni atom, ''direct'' electron spectroscopy would detect this, as is clearly observed in the prior valence-band photoemission[9–11] and inverse photoemission[12] studies. Note from Fig. 3 that a substantial portion of the Ni $3d$ radial distribution function extends beyond a radius of 0.75 Å and therefore participates in itinerant electron phenomena.

The results presented here for Ni are very reminiscent of temperature-dependent photoemission results from metallic Cr.[25,26] In those prior studies, a temperature-independent Cr $3s$ multiplet splitting was observed[25] up to 715 K above the bulk Néel temperature. This Cr atomic magnetism persists, even though direct valence-band measurements of Cr reveal the loss of magnetic order on the length scale of 6 Å.[26]

We note here that a temperature-independent $3s$ photoemission peak has been observed previously for Mn $3s$ in MnO (Ref. 27) and for Fe $3s$ in metallic Fe (Ref. 28). MnO is a highly localized ionic system. The Mn^{2+} atomic magnetic moment is not expected to vary from the antiferromagnetic to paramagnetic phase. So a temperature-independent Mn $3s$ photoemission peak is expected for MnO. Metallic Fe, though not as localized a system as MnO, is one of the stronger ''local moment'' systems of the itinerant magnets.[29,30] A temperature-independent Fe $3s$ line shape is therefore not too surprising. However, a temperature-independent Ni $3s$ line shape is surprising, since metallic Ni is not considered to be a strong local moment system,[29,30] and its exchange-split valence electronic structure shows a ''collapsing'' behavior above T_c, as discussed previously.

IV. CONCLUSIONS

An HRXPS study of the Ni $3s$ core level is presented. Nickel $3s$ HRXPS spectra measured at $T=298$ K ($T=0.47T_c$) and 863 K ($T=1.37T_c$) show the same spectral line shape. These HRXPS results, combined with prior spin-resolved x-ray photoelectron spectroscopy studies of Ni core levels, indicate the persistence of atomic magnetism in the paramagnetic phase of Ni on the length scale of ~0.75 Å. The data suggest that temperature-induced changes in the Ni $3d$ spin polarization occur at the periphery of the metallic atom, i.e., outside a radius of 0.75 Å, leaving the spin density within 0.75 Å unaffected. It is our hope that the data generate theoretical interest in the intra-atomic spatial variation of Ni spin polarization during the ferromagnetic-to-paramagnetic phase transition.

ACKNOWLEDGMENTS

This paper is based upon work supported by the National Science Foundation under Grant No. CHE-9117138.

[1] S. Hufner and G. K. Wertheim, Phys. Lett. **51A**, 301 (1975).
[2] S. J. Oh, J. W. Allen, I. Lindau, and J. C. Mikkelsen, Jr., Phys. Rev. B **26**, 4845 (1982).
[3] A. K. See and L. E. Klebanoff, Phys. Rev. Lett. **74**, 1454 (1995).
[4] L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B **8**, 2392 (1973).
[5] A. R. Williams and N. D. Lang, Phys. Rev. Lett. **40**, 954 (1978).
[6] G. van der Laan, M. Surman, M. A. Hoyland, C. F. J. Flipse, B. T. Thole, Y. Seino, H. Ogasawara, and A. Kotani, Phys. Rev. B **46**, 9336 (1992).
[7] B. T. Thole and G. van der Laan, Phys. Rev. Lett. **67**, 3306 (1991).
[8] R. Allenspach, D. Mauri, M. Taborelli, and M. Landolt, Phys. Rev. B **35**, 4801 (1987).
[9] D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. **40**, 1514 (1978).
[10] H. Hopster, R. Raue, G. Guntherodt, E. Kisker, R. Clauberg, and M. Campagna, Phys. Rev. Lett. **51**, 829 (1983).
[11] D.-P. Kamper, W. Schmitt, D. A. Wesner, and G. Guntherodt, Appl. Phys. A: Solids Surf. **49**, 573 (1989).
[12] M. Donath and V. Dose, Europhys. Lett. **9**, 821 (1989).
[13] P. Aebi, T. J. Kreutz, J. Osterwalder, R. Fasel, P. Schwaller, and L. Schlapbach, Phys. Rev. Lett. **76**, 1150 (1996).
[14] E. P. Wohlfarth, Rev. Mod. Phys. **25**, 211 (1953).
[15] V. Korenman and R. E. Prange, Phys. Rev. Lett. **53**, 186 (1984).
[16] J. Braun, G. Borstel, and W. Nolting, Phys. Rev. B **46**, 3510 (1992).
[17] A. Kakizaki, J. Fujii, K. Shimada, A. Kamata, K. Ono, K.-H. Park, T. Kinoshita, T. Ishii, and H. Fukutani, Phys. Rev. Lett. **72**, 2781 (1994).
[18] B. Sinkovic, L. H. Tjeng, N. B. Brookes, J. B. Goedkoop, R. Hesper, E. Pellegrin, F. M. F. de Groot, S. Altieri, S. L. Hulbert, E. Shekel, and G. A. Sawatzky, Phys. Rev. Lett. **79**, 3510 (1997).
[19] For an excellent review, see L. C. Davis, J. Appl. Phys. **59**, R25 (1986).
[20] J. G. Menchero, Phys. Rev. B **55**, 5505 (1997).
[21] A. K. See and L. E. Klebanoff, Phys. Rev. B **51**, 11 002 (1995).
[22] L. E. Klebanoff, D. G. Van Campen, and R. J. Pouliot, Phys. Rev. B **49**, 2047 (1994).
[23] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **17**, 911 (1991).
[24] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
[25] D. G. Van Campen, M. L. Knieriem, and L. E. Klebanoff, Phys. Rev. B **43**, 11 668 (1991).
[26] L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **31**, 6379 (1985).
[27] B. Hermsmeier, J. Osterwalder, D. J. Friedman, and C. S. Fadley, Phys. Rev. Lett. **62**, 478 (1989).
[28] C. S. Fadley and D. A. Shirley, Phys. Rev. A **2**, 1109 (1970).
[29] See, for example, A. Ziegler, Phys. Rev. Lett. **48**, 695 (1982) and references therein.
[30] See Fig. 2.10 from T. Moriya, in *Metallic Magnetism*, edited by H. Capellmann (Springer-Verlag, Berlin, 1987), p. 39.