Dichroism in the $3p$ Photoionization of Polarized Cr Atoms

A. von dem Borne, T. Dohrmann, A. Verweyen, and B. Sonntag
II. Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany

K. Godehusen and P. Zimmermann
Institut für Strahlungs-und Kernphysik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany
(Received 20 January 1997)

The $3p$ photoionization of polarized Cr atoms was investigated by means of photoelectron spectroscopy with linearly polarized vacuum ultraviolet undulator radiation. The $3p$ photoelectron spectra depend strongly on the polarization of the Cr ground state. Linear dichroism and linear magnetic dichroism in the angular distribution were observed using either linearly or circularly polarized laser radiation to polarize the ground state of the Cr atoms. Both effects provide striking confirmation of the general theory of photoionization from polarized atoms and elucidate recent results on magnetic thin films. [S0031-9007(97)03268-7]

PACS numbers: 32.80.Fb, 32.80.Hd

Because of their basic and practical importance the magnetic properties of multilayer systems and of ultrathin films on ferromagnetic substrates are currently the focus of many experimental and theoretical investigations [1,2]. Core photoelectron spectroscopy, exploiting linear or circular magnetic dichroism yields detailed and site-specific information. The pioneering experiments on the $2p$ shell of Fe [3] were quickly followed by a series of energy, angle, and spin resolved photoelectron studies using linearly or circularly polarized synchrotron radiation [4–7]. Thin layers of Cr or Mn on ferromagnetic substrates, or sandwiched between magnetic layers, are especially fascinating because their properties vary between antiferromagnetic and ferromagnetic and their half-filled $3d$ shells can provide large magnetic moments [1,8,9]. The models proposed for the interpretation of the spectra had to cope with the complexities produced by the interplay of the intraatomic and interatomic interactions ([10,11] and references therein). The strong $3p$-$3d$ coupling makes this especially difficult for the $3p$ photoelectron spectra of the $3d$-transition metals. Corresponding experiments on free aligned, or oriented, atoms open up the possibility to disentangle the atomic and the solid state effects. Previous $3p$ photoelectron spectra of the $3d$-transition metal atoms have only been observed for unpolarized atoms [12,13]. Now we have succeeded in determining the linear dichroism and the linear magnetic dichroism in the $3p$ photoelectron spectra of laser aligned/oriented ground state Cr atoms combining intense laser and vacuum ultraviolet (VUV) undulator radiation. Atomic Cr is a key element of the $3d$-transition metal series because of the strong many-electron effects exhibited in the core level spectra. The half-filled $3d$ and $4s$ shells make Cr amenable to a description with modern many-body theories [14]. The linear dichroism (LD) and the linear magnetic dichroism in the angular distribution (LMDAD) of the photoelectrons give detailed insight in the photoionization process by providing both the relative amplitudes and phases of the outgoing photoelectron waves [15,16].

The LD and LMDAD in the direct $3p$ photoionization of aligned and oriented Cr atoms were investigated for photon energies of 76 and 103 eV using highly polarized laser and undulator radiation on the U1-TGM6 beam line at BESSY (Berlin). The Cr atoms, produced by a resistively heated furnace, were aligned or oriented by laser pumping one of the Cr $3d^5 4s^7S_3 \rightarrow 3d^5 4p^7P_{2,3,4}$ transitions with linearly, or circularly, polarized laser radiation. The counterpropagating laser and undulator beams interact with the Cr atoms in the source volume of a 180° cylindrical mirror analyzer (CMA). The kinetic energy of the photoelectrons emitted at angles close to the magic angle ($\Theta_{\mathrm{CMA}} = 54.7°$) relative to the polarization axis of the undulator radiation was analyzed with an energy resolution of 0.8% of the pass energy. More details can be found in Refs. [14,17].

The linear dichroism is defined as the difference between two photoelectron spectra recorded for two perpendicular directions of the atomic alignment A_{20} produced by linear polarized laser light either parallel or perpendicular to the polarization axis of the VUV beam: $\mathrm{LD} = I(\|) - I(\perp)$. This effect is independent of the experimental geometry and can also be observed with an angle-integrating electron spectrometer. The linear magnetic dichroism in the angular distribution is defined as the difference between two spectra recorded for two atomic orientations A_{10} of the opposite sign, produced alternately by right and left circular polarized laser radiation: $\mathrm{LMDAD} = I(\uparrow) - I(\downarrow)$. In contrast to LD this effect can be observed only in angle-resolved spectra. For comparison with other experiments and theoretical results it is useful to normalize the LD and the LMDAD to the cross section and polarization of the atoms and the undulator radiation, which leads to the following relations

for the asymmetry parameters β_{LD} and β_{LMDAD}:

$$\beta_{\mathrm{LD}} A_{20} P = \frac{I(\|) - I(\perp)}{I(\|) + 2I(\perp)}, \quad (1)$$

$$\beta_{\mathrm{LMDAD}} A_{10} P = \frac{I(\uparrow) - I(\downarrow)}{I(\uparrow) + I(\downarrow)}. \quad (2)$$

A_{10} and A_{20} are the orientation and the alignment of the atomic ground state and P is the degree of linear polarization of the undulator radiation. The asymmetry parameters are dynamical parameters that are directly connected with the complex dipole transition amplitudes.

The $3p$ photoelectron spectrum of unpolarized Cr atoms

$$\mathrm{Cr\ I}\ 3p^6 3d^5 4s\,{}^7S_3 + \hbar\omega \rightarrow$$
$$(\mathrm{Cr\ II}\ 3p^5 3d^5 4s\,{}^8P, {}^6P + \epsilon s, \epsilon d)^7 P_{2,3,4}$$

like the corresponding spectrum of Mn [12] is dominated by the strong exchange interaction which spreads the ^8P and ^6P lines over more than 10 eV.

The upper part of Fig. 1 shows the ^8P main line of aligned Cr atoms excited with linearly polarized undulator radiation ($\hbar\omega = 76$ eV). The Cr atoms were prepared in aligned ground states by pumping with laser radiation polarized linearly parallel or perpendicular to the undulator radiation. The three fine structure components $^8P_{9/2,7/2,5/2}$ at binding energies 46.32(5), 46.69(5), and 47.01(5) eV are well separated. The solid lines are superpositions of three Gaussians and a parabolic background. The FWHM of 0.3 eV of the Gaussians is due to the bandpass of the electron spectrometer and monochromator. The amplitude of all three lines depends strongly on the direction of the atomic alignment. The dichroism obtained by calculating the difference $I(\|) - I(\perp)$ is presented in the center part of Fig. 1 whereas the normalized LD, calculated from the experimental spectra including the background, is given in the lower part of Fig. 1.

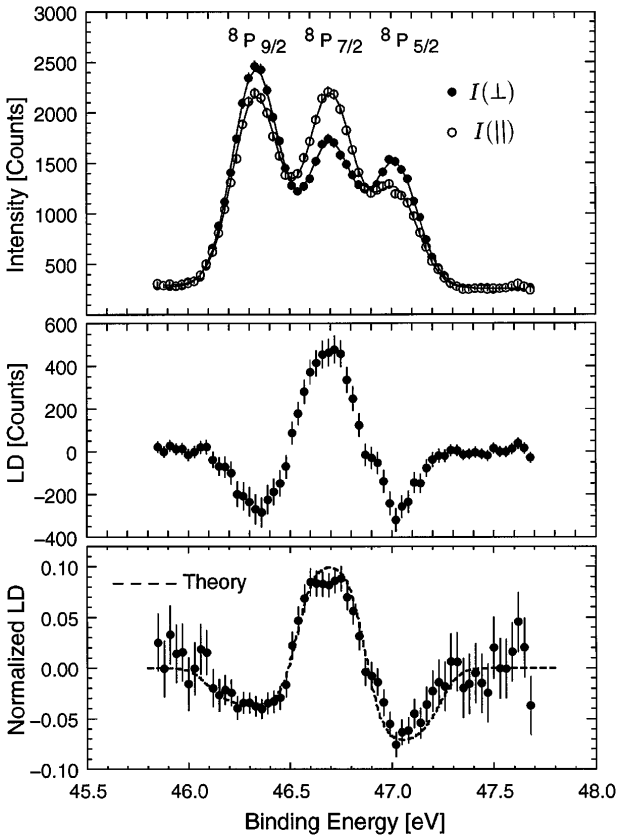

FIG. 1. The Cr $3p^5 3d^5 4s\,{}^8P\epsilon l$ photoelectron lines excited by linearly polarized VUV undulator radiation ($\hbar\omega = 76$ eV) for two perpendicular alignments of the atoms (upper part). The linear dichroism LD ($I[\|] - I[\perp]$) and the normalized LD $[(I[\|] - I[\perp])/(I[\|] + 2I[\perp])]$ are presented in the center and at the bottom, respectively.

The asymmetry parameters β_{LD} for the Cr II $^8P_{9/2,7/2,5/2}$ lines have been calculated for our experimental geometry by extending the results obtained by Dohrmann *et al.* [14] based on the theoretical description of the angular distribution of photoelectrons from polarized atoms [18]. In LS coupling, neglecting state multipoles higher than the aligment A_{20} the asymmetry parameters can be expressed as a function of the ratio $x = |D_s|/|D_d|$ of the reduced dipole matrix elements for the transitions to ϵs and ϵd continuum states.

$$\beta_{\mathrm{LD}} = C_J \frac{x^2 + 1/10}{x^2 + 1}. \quad (3)$$

If the dipole elements D_s and D_d are determined by the orbital momenta of the ion and the outgoing electron the coefficients C_J depend simply on the total angular momentum J of the residual Cr II $^8P_{9/2,7/2,5/2}$ ion ($C_{9/2} = -\frac{1}{4\sqrt{3}}$, $C_{7/2} = +\frac{5}{7\sqrt{3}}$, $C_{5/2} = -\frac{15}{28\sqrt{3}}$). For comparison with the experimental results the normalized LD was calculated using the β_{LD} obtained from Eq. (3) and taking into account the relative strengths of the lines, the experimental widths, the values for A_{20} and P, and the background. The curve obtained for $A_{20} = 0.4$, $P = 0.9$, and $|D_s|/|D_d| = 2$ is given by the dashed line in the lower part of Fig. 1. The calculated curve describes the experimental values very well. Despite the good agreement there is considerable uncertainty in the ratio of the dipole elements $|D_s|/|D_d| = 2.0 \pm {}^{1}_{0.5}$ extracted from the data. This is due to the limited accuracy of the values for $P = 0.90 \pm 0.05$ and $A_{20} = 0.40 \pm 0.05$. The strong dichroism demonstrates that transitions to s states contribute significantly to Cr $3p$ photoionization at this photon energy.

The results obtained for the ^8P main line of oriented Cr atoms, excited by linearly polarized undulator radiation ($\hbar\omega = 76$ eV) are presented in Fig. 2. The upper part shows two spectra recorded for atoms prepared in states with opposite orientation A_{10} by laser pumping with left, or right, circularly polarized laser light. The amplitudes of the fine structure components vary significantly upon changing the orientation of the atoms. The LMDAD is

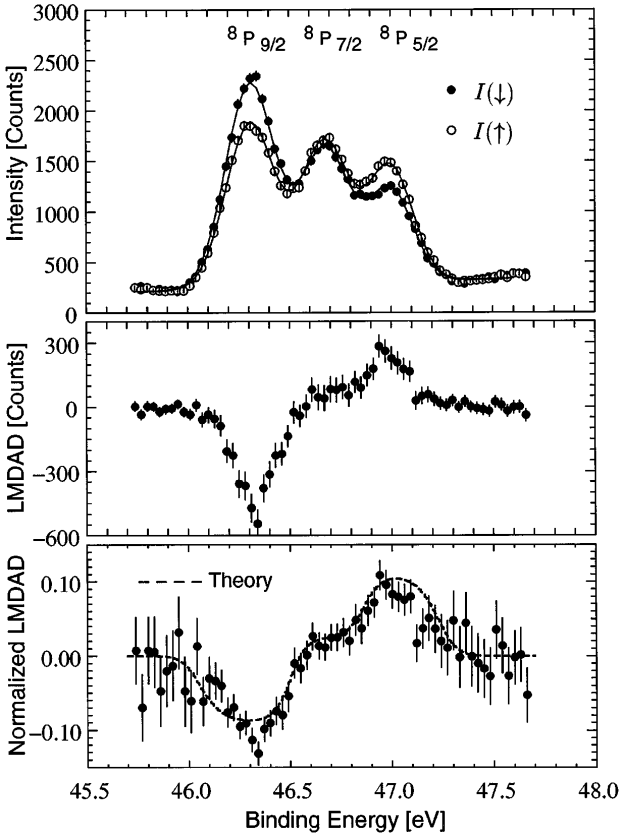

FIG. 2. The Cr $3p^5 3d^5 4s\,^8P\epsilon l$ photoelectron lines excited by linearly polarized VUV undulator radiation ($\hbar\omega = 76$ eV) for two opposite orientations of the atoms (upper part). The linear magnetic dichroism in the angular distribution LMDAD ($I[\uparrow] - I[\downarrow]$) and the normalized LMDAD $[(I[\uparrow] - I[\downarrow])/(I[\uparrow] + I[\downarrow])]$ are presented in the center and at the bottom, respectively.

depicted in the center part and the normalized LMDAD in the lower part of Fig. 2. The LMDAD differs markedly from the LD shown in Fig. 1. The LD is negative for the $^8P_{9/2,5/2}$ lines and positive for the $^8P_{7/2}$ line whereas the LMDAD is close to zero for this line and displays values of the opposite sign for the $^8P_{9/2}$ and $^8P_{5/2}$ lines. The calculations of the asymmetry parameters β_{LMDAD} were based on the approach successfully used to describe the LD. *LS* coupling was assumed to hold and state multipoles higher than the orientation A_{10} were neglected. The relation

$$\beta_{\mathrm{LMDAD}} = C_J \sin(\delta_s - \delta_d)\,\frac{x}{x^2 + 1} \qquad (4)$$

is very similar to Eq. (3) describing β_{LD}. The coefficients C_J ($C_{9/2} = -\frac{3}{\pi}$, $C_{7/2} = +\frac{6}{7\pi}$, and $C_{5/2} = +\frac{27}{7\pi}$) only depend on the total angular momentum of the Cr II ion and $x = |D_s|/|D_d|$ gives the ratio of the dipole matrix elements. In contrast to the β_{LD} the β_{LMDAD} depend on the phase difference of the continuum states. Since spin-orbit interaction of the continuum ϵd states is negligibly small only the phase difference $(\delta_s - \delta_d)$ between the ϵs and ϵd states enters. Good agreement with the experimental data has been achieved with the following parameters: $x = 2$, $\sin(\delta_s - \delta_d) = 0.95$, $A_{10} = 0.3$, and $P = 0.9$. The normalized LMDAD calculated in the same way as outlined for the normalized LD is given by the dashed line in the lower part of Fig. 2. Again there is considerable uncertainty in the values $x = 2.0 \pm {}^{1}_{0.5}$ and $\sin(\delta_s - \delta_d) = 0.95 \pm 0.05$ extracted from the experimental data due to the uncertainties in the values of the polarization $P = 0.90 \pm 0.05$ and the orientation $A_{10} = 0.30 \pm 0.05$. It is important to note that the values for x extracted from the LD and LMDAD measurements are consistent. Hartree-Fock calculations predict a ratio of $x = 3$ and $\sin(\delta_s - \delta_d) = 0.95$ [19] compatible with the experimental results. Since the photon energy of 76 eV is close to the Cooper minimum in the $3p \rightarrow \epsilon d$ cross section the $3p \rightarrow \epsilon s$ channel is expected to dominate.

The spectra of the normalized LD and LMDAD (lower parts of Figs. 1 and 2) indicate that in our case the dichroism disappears if one integrates over all fine structure components. In terms of the coefficients C_J (Eqs. (3) and (4)) we find the sum rule

$$\sum_J C_J(2J + 1) = 0\,, \qquad (5)$$

where the summation extends over all fine structure components characterized by the total angular momentum of the ion. Stimulated by our findings Kabachnik derived a more general formulation which confirms our results for initial states with zero orbital momentum [20].

The upper part of Fig. 3 shows the $3p$ photoelectron spectra of oriented Cr atoms recorded at a photon energy of 103 eV. Three eV above the ^8P line lies the lowest ^6P line assigned to the Cr II $[(3p^5\,^2P)\,(3d^5\,^4D)4s]^6P$ state of the ion. At this energy the fine structure of the lines is not resolved by the CMA. Both lines display a significant dependence on the orientation of the atoms. The LMDAD is given in the center part and the normalized LMDAD in the lower part of Fig. 3. In comparison to the LMDAD of the ^8P line the maxima and minima of the LMDAD in the ^6P line are interchanged. Since the calculated β_{LMDAD} values for the $^6P_{7/2,5/2,3/2}$ lines are very close to those of the $^8P_{9/2,7/2,5/2}$ lines this indicates an inverted ordering of the fine structure components. This has been confirmed by recent atomic calculations [19]. Except for the region around 48.5 eV the experimental normalized LMDAD is well described by the spectrum calculated for the parameters $x = 1$, $\sin(\delta_s - \delta_d) = 0.90$, $A_{10} = 0.3$, and $P = 1.0$. The decrease of x and $\sin(\delta_s - \delta_d)$ with increasing photon energy is in agreement with atomic calculations [19] which predict $x = 1$ and $\sin(\delta_s - \delta_d) = 0.85$ at 103 eV photon energy. The experiment, within the uncertainties [$x = 1.0 \pm 0.5$, $\sin(\delta_s - \delta_d) = 0.9 \pm 0.1$], confirms the predicted energy dependence.

The two photoelectron spectra $I(\uparrow)$ and $I(\downarrow)$ in the range of the ^8P line closely resemble the corresponding spectra

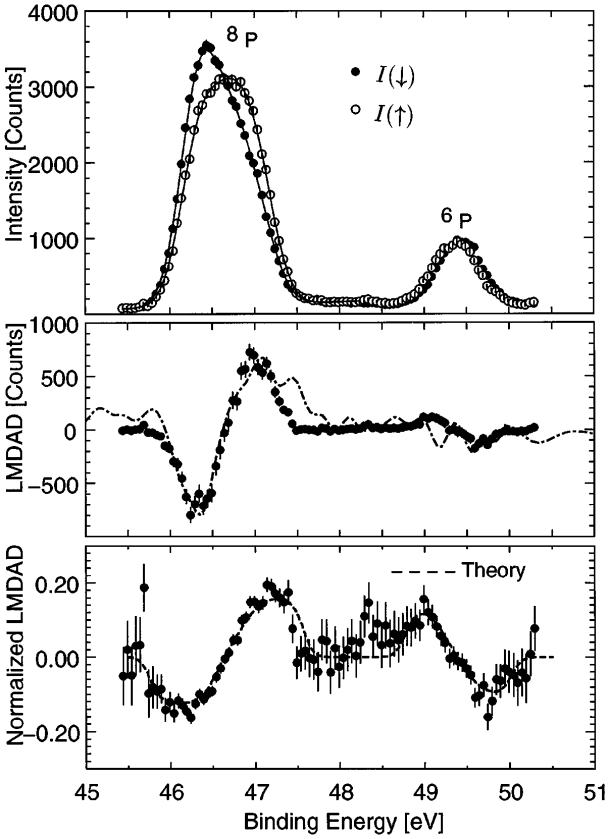

FIG. 3. The Cr $3p^5 3d^5 4s\,{}^8P, {}^6P\epsilon l$ photoelectron lines excited by linearly polarized VUV undulator radiation ($\hbar\omega = 103$ eV) for two opposite orientations of the atoms (upper part). The LMDAD ($I[\uparrow] - I[\downarrow]$) and the normalized LMDAD $[(I[\uparrow] - I[\downarrow])/(I[\uparrow] + I[\downarrow])]$ are presented in the center and bottom parts, respectively. The LMDAD determined for a thin Cr film on a Fe(100) surface [1] is included in the center.

for ferromagnetic bulk metals, or thin films, which also display an asymmetric line at lower binding energies and a broader, more symmetric line at higher binding energies [1,8,9]. The LMDAD of a thin Cr layer on a Fe(100) crystal surface [1] is given by the dash-dotted curve in the center of Fig. 3. The amplitude has been matched to the atomic LMDAD and the curve has been shifted in energy to correct for the different binding energies. The striking similarity between the two curves clearly demonstrates the atomic character of the effect. Furthermore it shows that a description within a single-particle approximation, which ascribes the splitting of the final state to the splitting of the $3p$ core hole is inadequate. We conclude that the correct description of core-level dichroism in $3d$ transition metals has to be formulated by taking proper consideration of the ionic states. For a detailed comparison with the results obtained for thin films the exact structure of the films and admixture of different atomic configurations have to be taken into account.

The authors thank J. E. Hansen and N. M. Kabachnik for stimulating discussions, M. Grothe and I. Schubert for their help during the measurements, and the BESSY staff for assistance. The financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] G. Rossi, F. Sirotti, and G. Panaccione, in *Magnetic Ultrathin Films, Multilayers and Surfaces, San Francisco, 1995*, edited by E. Marinero *et al.*, MRS Symposia Proceedings No. 384 (Material Research Society, Pittsburgh, 1995), p. 447.
[2] D. J. Huang, D. M. Riffe, and J. L. Erskine, Phys. Rev. B **51**, 15 170 (1995).
[3] L. Baumgarten, C. M. Schneider, H. Petersen, F. Schäfers, and J. Kirschner, Phys. Rev. Lett. **65**, 492 (1990).
[4] Ch. Roth, F. U. Hillebrecht, H. B. Rose, and E. Kisker, Phys. Rev. Lett. **70**, 3479 (1993).
[5] Ch. Roth, H. B. Rose, F. U. Hillebrecht, and E. Kisker, Solid State Commun. **86**, 647 (1993).
[6] F. Sirotti and G. Rossi, Phys. Rev. B **49**, 15 682 (1994).
[7] G. Rossi, F. Sirotti, N. A. Cherepkov, F. Combet Farnoux, and G. Panaccione, Solid State Commun. **90**, 557 (1994).
[8] Z. Xu, Y. Liu, P. D. Johnson, and B. S. Itchkawitz, Phys. Rev. B **52**, 15 393 (1995).
[9] Ch. Roth, Th. Kleemann, F. U. Hillebrecht, and E. Kisker, Phys. Rev. B **52**, R15 691 (1995).
[10] G. van der Laan, Phys. Rev. B **51**, 240 (1995).
[11] N. A. Cherepkov, Phys. Rev. B **50**, 13 813 (1994).
[12] J. Jiménez-Mier, M. O. Krause, P. Gerard, B. Hermsmeier, and C. S. Fadley, Phys. Rev. A **40**, 3712 (1989).
[13] R. Malutzki, M. S. Banna, W. Braun, and V. Schmidt, J. Phys. B **18**, 1735 (1985).
[14] Th. Dohrmann, A. von dem Borne, A. Verweyen, B. Sonntag, M. Wedowski, K. Godehusen, P. Zimmermann, and V. Dolmatov, J. Phys. B **29**, 4641 (1996).
[15] O. Plotzke, G. Prümper, B. Zimmermann, U. Becker, and H. Kleinpoppen, Phys. Rev. Lett. **77**, 2642 (1996).
[16] N. A. Cherepkov, V. V. Kuznetsov, and V. A. Verbitskii, J. Phys. B **28**, 1221 (1995).
[17] Th. Dohrmann, A. von dem Borne, A. Verweyen, B. Sonntag, M. Wedowski, K. Godehusen, and P. Zimmermann, J. Phys. B **29**, 5699 (1996).
[18] S. Baier, A. N. Grum-Grzhimailo, and N. M. Kabachnik, J. Phys. B **27**, 3363 (1994).
[19] J. E. Hansen (private communication).
[20] N. M. Kabachnik (private communication).