Soft x-ray magnetic circular dichroism study of Cr tellurides

Koichiro Yaji[a)] and Akio Kimura
*Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima
739-8526, Japan*

Michie Koyama
Kure National College of Technology, Agaminami 2-2-11, Kure 737, Japan

Chiyuki Hirai
*Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima
739-8526, Japan*

Hitoshi Sato and Kenya Shimada
*Hiroshima Synchrotron Radiation Center, Hiroshima University, 2–313 Kagamiyama, Higashi-Hiroshima
739-8526, Japan*

Arata Tanaka
*Department of Quantum Matter, ADSM, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima
739-8526, Japan*

Masaki Taniguchi
*Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526,
Japan; Hiroshima Synchrotron Radiation Center, Hiroshima University, 2-313 Kagamiyama,
Higashi-Hiroshima 739-8526, Japan*

(Presented on 9 November 2004; published online 28 April 2005)

Ferromagnetic chromium tellurides Cr_5Te_6 ($\delta=0.17$) and Cr_2Te_3 ($\delta=0.33$) have been investigated by Cr $2p$ x-ray absorption spectroscopy and x-ray magnetic circular dichroism (XMCD). The observed XMCD spectra have been analyzed by means of a configuration-interaction cluster model calculation. From calculated results, we suggest that the doped holes created by the Cr deficiency exist mainly in the Te $5p$ orbital of $Cr_{1-\delta}Te$. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854992]

Chromium chalcogenides $Cr_{1-\delta}X$ ($X=S,Se,Te$) with metal-deficient NiAs type crystal structure show various magnetic and electronic properties depending on X atoms and the vacancy concentration.[1] Among them, $Cr_{1-\delta}Te$ is a ferromagnet with metallic conductivity with Curie temperatures of 170–360 K, where the magnetic and electronic properties are different depending on δ. Extensive studies on the magnetism and the electronic specific heat coefficients have been performed so far.[2–4] To understand these properties, the band-structure calculation and the photoemission spectroscopy have been done.[5,6] In the photoemission spectroscopy experiments studied by Shimada *et al.*, while the overall features of the photoemission spectra agree with the calculated density of states, the satellite structure of the photoemission spectra, which does not appear in the band calculation is reproduced if the electronic correlation effect is taken into account.[6] Therefore, it is understood that these materials have the both localized and delocalized characters.

The x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) experiments are powerful tools to investigate the element specific electronic structure. One can examine the intersite hybridization between a transition metal and surrounding anions, by means of line-shape analyses of the XAS and XMCD spectra. In this study, we have performed Cr $2p$ core excited XAS and

XMCD experiments of $Cr_{1-\delta}Te$ ($\delta=0.17$ and 0.33) and have analyzed the experimental spectra with using a configuration interaction cluster model calculation to understand how the electronic structure are related to δ.

Cr $2p$ XAS and XMCD spectra were measured at BL25SU of SPring-8 by means of a total photoelectron yield method excited with a circularly polarized undulator radiation.[7–10] The XMCD spectra were taken for a fixed helicity of light by reversing the applied magnetic field at each $h\nu$. The external magnetic field was ~1.4 T at the sample position. A clean surface was obtained by *in situ* scraping of the samples with a diamond file under the ultra high vacuum condition (3×10^{-8} Pa). The temperature during the measurement was set at 110 K. The photon energy resolution was set to $E/\Delta E=5000$ for the Cr $2p$ core excitation energy.

The Cr $2p$ XAS (I_+ and I_-) spectra of Cr_5Te_6 ($\delta=0.17$) are shown in Fig. 1, where I_+ and I_- represent the absorption spectra for the direction of magnetization (which is opposite to the direction of the majority spin) parallel and antiparallel to the photon helicity, respectively. The $2p_{3/2}$ and the $2p_{1/2}$ core absorption peaks are located at about 576 and 585 eV. We can recognize that the intensity of I_+ is larger than that of I_- in the $2p_{3/2}$ core absorption region, whereas the intensity of I_+ is smaller than that of I_- in the $2p_{1/2}$ region. Figures 2(a) and 2(c) exhibit the experimental Cr $2p$ XMCD spectra (defined as I_+-I_-) of Cr_5Te_6 ($\delta=0.17$) and Cr_2Te_3 ($\delta=0.33$). The XMCD spectrum of Cr_5Te_6 shows the plus–minus fea-
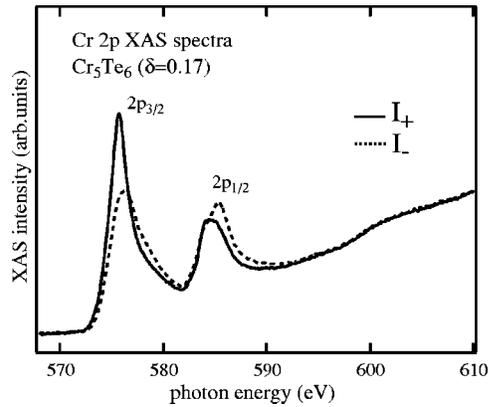
[a)]Electronic mail: koutay@hiroshima-u.ac.jp

FIG. 1. Cr $2p$ XAS spectra (I_+ and I_-) of Cr_5Te_6 with different helicities of incident radiation.

ture with increasing $h\nu$ as denoted by A and B at the $2p_{3/2}$ edge and the minus–plus–minus feature as indicated by C, D, and E at the $2p_{1/2}$ edge. The XMCD spectrum of Cr_2Te_3 shows a shoulder F on the lower energy side of the structure A, while overall features (A–E) are similar to those of Cr_5Te_6.

In order to evaluate several physical parameters that control the physical properties of chromium telluride, we have analyzed the experimental spectra by means of a configuration interaction (CI) cluster model calculation with full multiplets assuming a $[CrTe_6]^{10-}$ cluster. In this calculation, we have considered only with Te ions which are the first nearest neighbors for Cr ions, while the effect of the second nearest neighbor Cr ions have been neglected. A detailed procedure
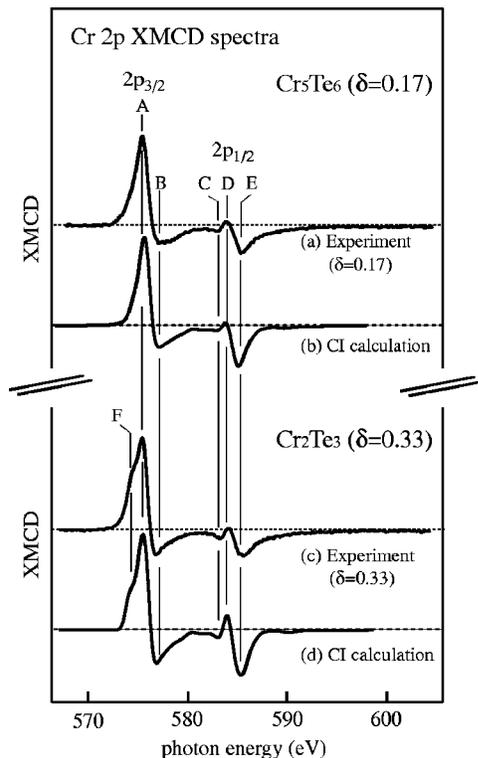

FIG. 2. (a), (c) The experimental Cr $2p$ XMCD spectra of Cr5Te6 ($\delta=0.17$) and Cr_2Te_3 ($\delta=0.33$), respectively. (b), (d) The calculated XMCD spectra by means of the CI cluster model.

of this calculation is shown elsewhere.[11] Here, the nominal d electron numbers in Cr_5Te_6 ($\delta=0.17$) and Cr_2Te_3 ($\delta=0.33$) are 3.60 and 3.00 per Cr atom, respectively, when we assume the Te valence to be $2-$. We have assumed the nominal d^3 configuration and have employed three more charge-transfer states such as $d^4\underline{L}, d^5\underline{L}^2$ and $d^6\underline{L}^3$, where $\underline{L}$ denotes a hole in Te $5p$ orbital. Thus the initial state is expanded by a linear combination of $d^3, d^4\underline{L}, d^5\underline{L}^2, d^6\underline{L}^3$. To perform the CI calculation, four adjustable parameters are introduced as follows: the charge-transfer energy $\Delta \equiv E(d^4\underline{L}) - E(d^3)$, the Coulomb interaction energy U_{dd} between the $3d$ electrons, the hybridization energy $V_{e(g)}$ $[=-\sqrt{3}(pd\sigma)]$ and the octahedral crystal field splitting $10Dq$. The calculated XMCD spectra of Cr_5Te_6 and Cr_2Te_3 are shown in Figs. 2(b) and 2(d), respectively. We find that the calculated spectra reproduce not only the dispersive XMCD feature at the $2p_{3/2}$ edge (A and B), but also the structures at the $2p_{1/2}$ edge including the small positive structure found in the lower $h\nu$ region (C, D, and E) with the following parameters: $\Delta=-2.0$ eV, $U_{dd}=2.3$ eV, $V_{eg}=1.3$ eV, and $10Dq=0.7$ eV for Cr_5Te_6 and $\Delta=-1.5$ eV, $U_{dd}=2.3$ eV, $V_{eg}=1.3$ eV, and $10Dq=1.0$ eV for Cr_2Te_3. The $U_{dd}=2.3$ eV has been estimated from the Cr $M_{23}VV$ Auger-electron spectra and the self convolution of the Cr $3d$-derived spectra.[6] The value of $V_{eg}=1.3$ eV $[(pd\sigma)=-0.75$ eV$]$ has been evaluated by using the formula $(pd\sigma)=\eta_{pd\sigma}(\hbar^2/m)(r_d^{1.5}/d^{3.5})$ with $\eta_{pd\sigma}=-2.95$ and $r_d(Cr)=0.9$ Å.[12]

We have obtained the similar parameter values of Δ, U_{dd}, V_{eg}, and $10Dq$ for Cr_5Te_6 and Cr_2Te_3, indicating that the local Cr $3d$ electronic states are not much affected by the Cr deficiency δ. Here, we notice that the negative Δ value is obtained for Cr_5Te_6 and Cr_2Te_3, suggesting that the lowest-energy state is not dominated by the d^3 state, but by the $d^4\underline{L}$. The calculated result also shows that the averaged $3d$ electron number is 4.5, which is larger than 4 (Cr^+). Thus we interpret that the doped holes created by the Cr deficiency do not stay in the Cr $3d$ states but exist in the Te $5p$ orbitals for $Cr_{1-\delta}Te$. This result is supported by the band-structure calculation of $Cr_{1-\delta}Te$, where the hole pocket derived from the Te $5p$ state appears around Γ point in the Brillouin zone when the Cr vacancy is introduced in the material.[5]

In summary, we have experimentally studied the Cr $2p$ XMCD spectra of Cr_5Te_6 and Cr_2Te_3. The observed changes with the Cr vacancy in the XMCD spectra are found to be small. We have obtained the physical parameters Δ, U_{dd}, V_{eg}, and $10Dq$ by the analysis of the experimental spectra on the basis of the CI cluster model calculation. It is concluded from these results that the doped holes created by the Cr deficiency exist mainly in the Te $5p$ orbitals.

[1] K. Adachi and S. Ogawa, in *Landolt-Börnstein New Series III/27a*, edited by H. P. J. Wijn (Springer, Berlin, 1988), p. 99.
[2] F. K. Lotgering and E. W. Gorter, J. Phys. Chem. Solids **3**, 328 (1957).
[3] A. F. Andresen, Acta Chem. Scand. (1947-1973) **24**, 3495 (1970).

[4]F. Grønvold and E. F. Westrum, Jr., Z. Anorg. Allg. Chem. **328**, 272 (1964).

[5]J. Dijikstra, H. H. Weitering, C. F. van Bruggen, C. Haas, and R. A. de Groot, J. Phys.: Condens. Matter **1**, 9141 (1989).

[6]K. Shimada, T. Saitoh, H. Namatame, A. Fujimori, S. Ishida, S. Asano, M. Matoba, and S. Anzai, Phys. Rev. B **53**, 7673 (1996).

[7]S. Suga, S. Imada, A. Yamasaki, S. Ueda, T. Muro, and Y. Saitoh, J. Magn. Magn. Mater. **233**, 60 (2001).

[8]S. Suga, Nucl. Instrum. Methods Phys. Res. A **467–468**, 1388 (2001)

[9]Y. Saitoh, H. Kimura, Y. Suzuki, T. Nakatani, T. Matsushita, T. Muro, T. Miyahara, M. Fujisawa, K. Soda, S. Ueda, H. Harada, M. Kotsugi, A. Sekiyama, and S. Suga, Rev. Sci. Instrum. **71**, 3254 (2000).

[10]Y. Saitoh, H. Kimura, Y. Suzuki, T. Nakatani, T. Matsushita, T. Muro, T. Miyahara, M. Fujisawa, K. Soda, S. Ueda, A. Sekiyama, S. Imada, and S. Suga, Nucl. Instrum. Methods Phys. Res. A **467–468**, 553 (2001).

[11]A. Tanaka and T. Jo, J. Phys. Soc. Jpn. **63**, 2788 (1994).

[12]W. A. Harrison, *Electronic Structure and the Physical Properties of Solids* (Dover, New York, 1989)