Electronic structures of Cr$_{1-\delta}$X (X=S, Te) studied by Cr 2p soft x-ray magnetic circular dichroism

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(Dated: March 22, 2022)

Cr 2p core excited XAS and XMCD spectra of ferromagnetic Cr$_{1-\delta}$Te with several concentrations of $\delta=0.11-0.33$ and ferrimagnetic Cr$_5$S$_6$ have been measured. The observed XMCD lineshapes are found to very weakly depend on $\delta$ for Cr$_{1-\delta}$Te. The experimental results are analyzed by means of a configuration-interaction cluster model calculation with consideration of hybridization and electron correlation effects. The obtained values of the spin magnetic moment by the cluster model analyses are in agreement with the results of the band structure calculation. The calculated result shows that the doped holes created by the Cr deficiency exist mainly in the Te 5p orbital of Cr$_{1-\delta}$Te, whereas the holes are likely to be in Cr 3d state for Cr$_5$S$_6$.

I. INTRODUCTION

Chromium chalcogenides Cr$_{1-\delta}$X (X=S, Se, Te) with metal-deficient NiAs type crystal structures show various magnetic and electronic properties. Among them, chromium tellurides Cr$_{1-\delta}$Te are ferromagnets with metallic conductivity with Curie temperatures of 170-360K.

Cr$_{1-\delta}$Te with $\delta < 0.1$ form the hexagonal NiAs crystal structure, while Cr$_3$Te$_4$($\delta=0.25$) and Cr$_2$Te$_3$($\delta=0.33$) form the monoclinic and the trigonal crystal structures, where Cr vacancies occupy in every second metal layer. The ordered magnetic moments evaluated from the magnetization measurements show much smaller values such as 2.4-2.7$\mu_B$ for the Cr$_{1-\delta}$Te with $\delta < 0.1$, 2.35$\mu_B$ for Cr$_3$Te$_4$($\delta=0.25$) and 2.0$\mu_B$ for Cr$_2$Te$_3$($\delta=0.33$) than those expected from the ionic model. According to neutron-diffraction studies, the small value of saturation magnetization is partly explained if we take the spin canting into account for $\delta=0.25$. The magnetic moment induced on the Cr ion for $\delta=0.25$ is close to an integral number of Bohr magnetons, suggesting the existence of mixed valence Cr$^{3+}$. However for Cr$_2$Te$_3$($\delta=0.33$), the ordered magnetic moment of 2.65 - 2.70$\mu_B$, deduced from the neutron diffraction, is much smaller than that calculated using the ionic model, 3$\mu_B$, suggesting the itinerant nature of the d
Electron specific heat coefficients $\gamma$ are much dependent on $\delta$. The estimated $\gamma$ for Cr$_5$Te$_6$(δ=0.167), Cr$_5$Te$_4$(δ=0.25) and Cr$_2$Te$_3$(δ=0.33) are 10, 1 and 4 mJ/atom/K$^2$. The $\gamma$ for Cr$_5$Te$_4$ is quite close to the predicted value 1.0~1.4 mJ/atom/K$^2$ using the calculated density of states (DOS) at the Fermi level ($E_F$), while that for Cr$_2$Te$_3$ is much larger than the predicted one, $\gamma \sim 0.82 - 0.96$ mJ/atom/K$^2$. Such large $\gamma$ values suggest that electron correlation effects are also important in Cr$_5$Te$_6$ and Cr$_2$Te$_3$. The electron correlation effects in these "itinerant ferromagnets" Cr$_{1-x}$Te has been discussed with the photoemission spectra. It has been pointed out that the spectral weight in $E_B$=2-4eV observed in the photoemission spectra of Cr$_9$S$_4$Te and Cr$_3$Te$_4$ can not be explained by the theoretical band structure calculation, and the intensity at $E_F$ is found to be smaller than the theoretical DOS. On the other hand, the spectral weight in $E_B$=2-4eV has been reproduced with the configuration interaction cluster-model calculation, indicating the importance of the electron correlation effect in Cr$_{1-x}$Te.

In contrast to the telluride compounds, Cr$_{1-x}$S shows the antiferromagnetic structure and some of them present a metal-semiconductor transition. Among them, CrS$_6$ shows ferri-antiferromagnetic phase transition below 150K. In the ferrimagnetic phase above 150K, there appears a tiny net magnetic moment as a result of the anti-parallel spin alignment between the adjacent Cr atoms with slightly different magnetic moments. Recently, in the analogy of the perovskite manganites, a colossal magnetoresistance has been found for the sulfur deficient Cr$_2$S$_3$, which may contain both Cr$^{3+}$($d^3$) and Cr$^{2+}$($d^4$) ions.

There has been a study of electronic structure using a band structure calculation to clarify the several magnetic and electronic properties depending on $\delta$ and X atom of Cr$_{1-x}$X (X=S, Se, Te). The calculation has successfully described the antiferromagnetic ground state for CrS, whereas the ferromagnetic state has not been properly described for CrTe.

Here we present a Cr 2p soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) spectra of ferromagnetic Cr$_{1-x}$Te and ferrimagnetic Cr$_3$S$_6$. It is known that core XAS is a powerful tool to study the element specific valence electronic states of materials. XMCD in the core XAS spectrum provides us with useful information on the element specific spin and orbital magnetic moments with use of the "sum rule". It is widely known that the spectral shapes of the XAS and XMCD spectra are strongly dependent on the electronic states or the electronic configuration of the derived atom. Besides, these lineshapes can be remarkably affected by the intersite hybridization between the surrounding atoms or by the band structure of the crystal. In other words, the spectra can be a good fingerprint of the electronic states inside the crystals. For example, the valency (or the electron number) can be determined by the XAS and XMCD spectral lineshapes. One can also determine several physical parameters such as the Coulomb repulsion energy, the charge transfer energy as well as the hybridization energy from the analyses of experimental XAS and XMCD spectral lineshapes. In order to understand how the electronic states are related to the $\delta$ and X atom dependences of the magnetic and electronic properties, we have performed Cr 2p XAS and XMCD experiments of Cr$_{1-x}$Te and Cr$_3$S$_6$.

II. EXPERIMENTAL

Polycrystalline samples were synthesized from mixed powders of constituent elements. They were sealed in evacuated silica tubes, which were heated for a week at 1000°C. After this, the samples were ground and sealed in silica tubes again and heated for 2 hours at 1450°C and then cooled gradually to 1000°C and finally quenched into water. The stoichiometry and the homogeneity of Cr$_{1-x}$Te and Cr$_3$S$_6$ have been estimated by means of Electron Probe Micro-Analysis (EPMA). X-ray diffraction studies confirmed that all of the samples were in a single phase.

Cr 2p core absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) spectra were measured at BL25SU of SPring-8 in Japan. Circularly polarized light was supplied from a twin-helical undulator, with which almost 100% polarization was obtained at the peak of the first-harmonic radiation. After having set the two undulators to opposite helicity, helicity reversal was realized by closing one undulator and fully opening the other. Cr 2p XAS spectra were measured by means of the total photoelectron yield method by directly detecting the sample drain current while changing the photon energy $h\nu$. The photon energy resolution was set to $\Delta E = 5000$ for the Cr 2p core excitation regions. The measurement was performed in the Faraday geometry with both the incident light and the magnetization perpendicular to the sample surface. We used two pairs of permanent dipole magnets with holes for passing the excitation light. The external magnetic field of $\sim 1.4T$ at the sample position was alternately applied by setting one of the two dipole magnets on the optical axis by means of a motor-driven linear feedthrough. The XMCD spectra were taken for a fixed helicity of light by reversing the applied magnetic field at each $h\nu$. In the present paper, the XMCD spectrum is defined as $I_+ - I_-$, 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. Clean surfaces were obtained by in situ scraping of the samples with a diamond file under ultra high vacuum condition (3×10$^{-8}$ Pa). The cleanliness of the sample surfaces was first checked by the disappearance of a typical structure related to Cr oxides. We could also check the degree of contamination from the magnitude of the XMCD signal, because its ampli-
tude grew and finally saturated when the sample surface became clean enough. We considered that the unscraped or contaminated surface was covered with antiferromagnetic or paramagnetic compounds such as Cr$_2$O$_3$, which hardly contribute to the XMCD spectrum. It is generally known that the total photoelectron yield reflects the absorption spectrum in the core-excitation region. The temperatures during the measurement were ~110K for Cr$_{1.8}$Te and 200K for Cr$_3$S$_6$ (ferrimagnetic phase).

III. CI CLUSTER MODEL CALCULATION WITH FULL MULTIPLETS

The CI cluster model calculation has been done with a program code developed by A. Tanaka by means of the recursion method. The detailed procedures are described elsewhere. Slater integrals have been calculated by Cowan’s code and the calculated values are listed in Table II. In the calculation, the Slater integrals are scaled down to 80\% of the listed values to take into account intra-atomic relaxation effect.

IV. RESULTS AND DISCUSSION

The XAS and XMCD spectra in the Cr 2p core excitation region have been measured for Cr$_8$Te$_9$ ($\delta = 0.11$), Cr$_3$Te$_6$($\delta = 0.17$), Cr$_3$Te$_4$($\delta = 0.25$), Cr$_2$Te$_5$($\delta = 0.33$) and Cr$_3$S$_6$ ($\delta = 0.17$). The Cr 2p XAS ($I_+$ and $I_-$) spectra with both helicities of incident radiation and the XMCD ($I_+ - I_-$) spectra of Cr$_5$Te$_6$ are shown in Fig.1 (a) and (b). It is found that the $2p_{3/2}$ and the $2p_{1/2}$ core absorption peaks are located at about 576 and 585 eV, and the broad hump is found around the photon energy of 600-605 eV. Since the core level binding energies ($E_B$) of the Cr 2p and Te 3d levels are quite close to each other, one may expect the overlapping of these absorption edges. We expect much lower Te 3d $\rightarrow$ 5p absorption cross section ($\leq 5\%$) compared to that of the Mn 2p $\rightarrow$ 3d absorption as observed, i.e., in Te 4d $\rightarrow$ 5p absorption spectrum of MnTe$_2$.

We also expect that the observed Cr 2p XAS fine structures are almost unaffected by the Te 3d XAS spectrum because the Te 3d core absorption is expected to be very broad due to the wide conduction band derived from the itinerant nature of the Te 5p electrons. Therefore one can assume that the Te 3d core absorption spectrum behaves like a background and the observed XAS spectra in the present photon energy range mostly reflect the Cr 2p core absorption. However, the broad hump at 600-605 eV can be still assigned to the Te 3d $\rightarrow$ 5p absorption mainly because the observed XMCD asymmetry is negligible in this energy region. It is found 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. Besides, the spectral weight of $I_+$ is shifted to lower energy compared to $I_-$ in both $2p_{3/2}$ and $2p_{1/2}$ regions. This derives the complicated XMCD ($I_+ - I_-$) structures as shown by the solid line in Fig.1 (b). Here, the spectrum (solid line) shows remarkable XMCD with positive sign at the $2p_{3/2}$ core absorption edge ($h\nu=575.5\text{eV}$) as marked with A, which is followed by the smaller asymmetry with negative sign ($h\nu=578\text{eV}$) as represented by B. It is noticed that the XMCD signal does not reach zero even in the region between the spin-orbit split 2p components. There is still finite and negative XMCD on the lower energy side of the $2p_{1/2}$ absorption edge ($h\nu=583\text{eV}$). Then one finds a small positive ($h\nu=584\text{eV}$) and a large negative ($h\nu=585.5\text{eV}$) XMCD peaks with increasing $h\nu$ as marked with C, D and E in Fig.1 (b). To eliminate the possible instrumental asymmetries, we have taken the spectra by reversing the helicity of the incident radiation. As a result of this procedure, it is found that the observed XMCD signals with opposite helicities of the incident lights are quite symmetric with respect to the zero line as shown by the solid and dashed line. This means that the observed complicated structures of the XMCD spectrum are intrinsic.

In Fig.2, are shown the helicity averaged Cr 2p XAS spectra represented as ($I_+ + I_-)/2$ of (a)Cr$_8$Te$_9$ ($\delta = 0.11$), (b)Cr$_3$Te$_6$ ($\delta = 0.17$), (c)Cr$_3$Te$_5$ ($\delta = 0.25$), (d)Cr$_2$Te$_3$ ($\delta = 0.33$) and (e)Cr$_3$S$_6$ ($\delta = 0.17$). In contrast to the

![Figure 1](image1.png)

**FIG. 1:** (a) Cr 2p XAS spectra ($I_+$ and $I_-$) with different helicities of incident radiation. (b) XMCD spectrum ($I_+ - I_-$) of Cr$_5$Te$_6$ (solid line). The XMCD spectrum taken by reversing the helicity of the incident radiation is also shown (dashed line).
spectrum of Cr$_5$Te$_6$ (Fig. 2(b)), a shoulder is found on the higher $h\nu$ side of the 2$p_{3/2}$ edge in the spectrum of Cr$_6$Te$_9$. One also finds broad and small shoulder on the lower energy side of the 2$p_{1/2}$ peaks for $\delta=0.11$. In the cases of Cr$_{1-\delta}$Te with $\delta=0.17$, 0.25 and 0.33, the line width of the 2$p_{3/2}$ edge is narrower with some tail extending to the higher $h\nu$ compared to that for $\delta=0.11$. Besides, the shoulder on the lower $h\nu$ side of the 2$p_{1/2}$ edge has comparable spectral weight to that of the 2$p_{1/2}$ main peak in these spectra. In addition, the broad humps are observed in the $h\nu$ region of 600-605eV for all of the spectra as already pointed out for $\delta=0.17$. The Cr 2$p$ XAS spectrum of Cr$_5$S$_6$ shows a shoulder structure at the lower $h\nu$ of the 2$p_{3/2}$ main peak, which is absent in the spectra of Cr$_{1-\delta}$Te as shown in Fig. 2(e). Several structures are also found in the 2$p_{1/2}$ energy region.

The XMCD spectra obtained as $I_+ - I_-$ of Cr$_{1-\delta}$Te with $\delta=0.11$, 0.17, 0.25 and 0.33 are shown in Fig. 3. We find that the overall lineshape of the XMCD spectrum for $\delta=0.11$ is similar to that for $\delta=0.17$, in which all of the fundamental structures A-E are observed. This is not expected because the XAS spectrum for $\delta=0.11$ shows a different feature from that for $\delta=0.17$ as stated above. Therefore we speculate that the shoulder structure at the 2$p_{3/2}$ edge in the XAS spectrum for $\delta=0.11$ (Fig. 2(a)) is extrinsic and might come from the remaining part of the chromium oxide in the sample, which hardly contribute to the XMCD spectrum because of its non-ferromagnetic nature. For higher $\delta$, we find that the XMCD spectrum for $\delta=0.25$ resembles to that for $\delta=0.33$. It can be realized that the XMCD spectra for $\delta=0.25$ and 0.33 show a different feature from those for $\delta=0.11$ and 0.17, where the shoulder structure F is found on the low $h\nu$ side of the peak A and the negative structure B is sharper than those for $\delta=0.11$ and 0.17 as shown in Fig. 3.

First, we have tried to evaluate the contribution of the orbital magnetic moment $m_{\text{orb}}$ from the experimental XMCD spectra with the use of the following sum rule:

$$m_{\text{orb}} = \frac{4}{3} \int_{L_2+L_3} (I_+ - I_-) d\nu (10 - n_d) \tag{1}$$

where $n_d$ represents 3$d$ electron number. The estimated $m_{\text{orb}}$ value is turned out to be almost negligible, suggesting the quenched Cr 3$d$ orbital magnetic moment, in consistence with the measured $g$ value ($g \sim 2$). A determination of the spin magnetic moment using sum rules for lighter transition metal elements such as Cr is question-able because the 2$p_{3/2}$ and 2$p_{1/2}$ edges are not well separated and are mixed with each other. In this case, the best way to derive the spin magnetic moment $m_{\text{spin}}$ is to fit the calculated spectrum to the experimental one as will be discussed below.

Next, in order to evaluate several parameters that control the physical properties of Cr$_{1-\delta}$Te, we have calculated the Cr 2$p$ XAS and XMCD spectra by means of a configuration interaction (CI) cluster-model calculation with full multiplets assuming a [CrTe$_6$]$^{10-}$ cluster so as to reproduce the experimental spectra of Cr$_{1-\delta}$Te. Here, the nominal $d$ electron numbers in Cr$_6$Te$_9$(\(\delta=0.11\)), Cr$_5$Te$_6$(\(\delta=0.17\)), Cr$_3$Te$_4$(\(\delta=0.25\)) and Cr$_2$Te$_3$(\(\delta=0.33\)) are $\sim 3.75$, 3.60, 3.33 and 3.00 per Cr atom, respectively.
when we assume the Te valence to be 2−. We have employed four charge-transfer states such as $d^3$, $d^3L^2$, $d^3L^2$, and $d^5L^3$, where $L$ denotes a hole in the Te $5p$ orbital. Thus the initial state is expanded by a linear combination of these four states and the final state is described by a linear combination of $2pd^1$, $2pd^2L$, $2pd^6L^2$, and $2pd^7L^3$, where $2p$ denotes a core hole in the $2p$ core level in the absorption final state. Slater integrals and spin-orbit coupling constants for $d^3$, $d^3$, $d^2$, and $d^5$ configurations in the initial state and for $p^3d^1$, $p^3d^2$, $p^5d^0$, and $p^5d^0$ in the XAS final states are listed in Table II. To perform the CI calculation, four adjustable parameters are introduced as follows; the charge-transfer energy $\Delta \equiv E(d^4L) - E(d^3)$, the Coulomb interaction energy $U_{dd}$ between the $3d$ electrons, the Coulomb attraction energy $U_{cd}$ between the $2p$ core hole and $3d$ electron, the hybridization energy $V_{pd} = -\sqrt{3}(pd\sigma)$ and the octahedral crystal field splitting $10Dq$. There has been a claim that a truncated basis set using at most two configurations ($d^{n} + d^{n+1}L$) in the cluster model analysis would provide incorrect physical parameters especially for highly covalent materials with small $\Delta$ value that include a highly oxidized element (such as $M^{3+}$ or $M^{4+}$) if one compares it with the result using a complete basis set. Here we use four basis set that should be enough to obtain reasonable physical parameters, which would be confirmed from the result that the state with highest order ($=d^5L^3$) is found to show very small weight (<7%).

We have used the $U_{dd}$ $\sim 2.3$ eV, which has been estimated from the Cr $M_{23}VV$ Auger-electron spectra and the self-convolution of the Cr $3d$-derived spectra. The same value of $V_{pd} = 1.3$ eV [(pd$\sigma$) = $-0.75$ eV] has been considered, where it has been evaluated by using the formula $\eta_{pd\sigma} = \frac{h^2}{m} \cdot \frac{r_{d}^{1.5}}{d^{3.5}}$ with $\eta_{pd\sigma} = -2.95$ and $r_{d}$ (Cr) = $0.9$ Å. Here, $U_{cd}$ has been fixed to $U_{dd}/U_{cd} = 0.83$ and the relationship $(pd\sigma)/(pd\pi) = -2.0$ has been assumed.

For Cr$_{1-\delta}$Te with $\delta = 0.11$ and 0.17, we have adjusted the charge transfer energy $\Delta$ and $10Dq$ to fit the experimental XAS and XMCD spectra. Fig. 4 (b) and (d) show the calculated XAS and XMCD spectra with $\Delta$ = $-2.0$ eV and $10Dq$ = 0.7 eV, which are broadened by the Lorentzian and Gaussian functions with the FWHM of 0.6 eV for each. It is noticed that the calculated XAS spectrum fits well with the experimental spectrum for $\delta = 0.11$ and 0.17 including the shoulder structure in the $2p_{1/2}$ region. The calculated XMCD spectrum reproduces not only the dispersive XMCD feature at the $2p_{3/2}$ edge (A and B), but also the structures at $2p_{1/2}$ edge including the small positive structure found in the lower $hv$ region (C, D, and E) as shown in Fig. 4 (d). It is noted here that we have obtained the negative value of $\Delta$, which means that the ground state is not dominated by the $d^3$ state but by the $d^4L$ and $d^5L^2$ states because the energy differences $E(d^4L) - E(d^3)$ and $E(d^5L^2) - E(d^3)$ are expressed as $\Delta$ = $-2.0$ eV and $2\Delta + U_{dd}$ = $-1.7$ eV, respectively when the hybridization ($V_{pd}$) is off. That is, the most stable $d^4L$ state is formed by the charge transfer from the lig- and Te $5p$ orbitals to the Cr $3d$ orbitals. The calculated result also shows that the weight of $d^4L + d^5L^2$ exceeds 80%, which is due to the strong hybridization between Cr.
TABLE I: *Ab initio* Hartree-Fock values of the Slater integrals and spin-orbit coupling constants (in units of eV). In the actual calculation, the Slater integrals have been scaled to 80% of these values to take into account intra-atomic relaxation effect.

| configuration | $F^1(d,d)$ | $F^2(p,d)$ | $G^1(p,d)$ | $G^2(p,d)$ | $\xi(3d)$ | $\xi(2p)$ |
|---------------|------------|------------|------------|------------|-----------|-----------|
| Cr $d^3$      | 10.777     | 6.755      | –          | –          | 0.030     | –         |
| Cr $d^4$      | 9.649      | 6.002      | –          | –          | 0.030     | –         |
| Cr $d^5$      | 8.357      | 5.146      | –          | –          | 0.025     | –         |
| Cr $d^6$      | 6.910      | 4.205      | –          | –          | 0.021     | –         |
| Cr $p^3d^4$   | 11.596     | 7.270      | 6.526      | 4.788      | 2.722     | 0.047     |
| Cr $p^2d^5$   | 10.777     | 6.552      | 5.841      | 4.204      | 2.388     | 0.041     |
| Cr $p^2d^6$   | 9.303      | 5.738      | 5.151      | 3.644      | 2.069     | 0.035     |
| Cr $p^3d^7$   | 7.867      | 4.801      | 4.461      | 3.155      | 1.768     | 0.030     |

Table II: Parameters obtained from the analyses of the XAS and XMCD spectra of Cr$_3$Te$_3$ and Cr$_2$Te$_3$ with CI cluster model calculation (in units of eV). We assumed $U_{dd}/U_{cd} = 0.83$ and $(pdx)/(pd\sigma) = -2$.

|           | $\Delta$ | $10Dq$ | $U_{dd}$ | $pd\sigma$ | $n_d$ | $m_{spin}$ | $m_{orb}$ |
|-----------|----------|--------|----------|------------|-------|------------|-----------|
| Cr$_{1-x}$Te ($\delta=0.11, 0.17$) | -2.0 | 0.7 | 0.7 -0.75 | 4.5 | 3.6 | -0.2 |
| Cr$_{1-x}$Te ($\delta=0.25, 0.33$) | -1.5 | 1.0 | 0.7 -0.75 | 4.3 | 3.2 | -0.03 |
| Cr$_2$S$_6$ | 0.5 | 1.0 | 0.7 -0.87 | 3.8 | 3.1 | -0.05 |

The estimated $m_{spin}$ and $m_{orb}$ are 3.6$\mu_B$ and -0.02$\mu_B$, respectively. Such a quite small $m_{orb}$ stems from the dominant $d^5L^2$ configuration in the ground state and is consistent with the negligible value with use of the sum rule as mentioned above. The calculated $m_{spin}=3.6\mu_B$ is consistent with the values given by the band-structure calculation 3.3$\mu_B$\(^{18}\) but is much larger than the saturation magnetic moment $\sim2.5\mu_B$.

We have also applied the calculation to Cr$_{1-x}$Te with $\delta=0.25$ and 0.33. Figs.5 (b) and (d) show the calculated XAS and XMCD spectra with the parameters $\Delta=-1.5$eV and $10Dq=1.0$eV. We find a good correspondence between the calculated XAS/XMCD spectra and the experimental ones. We recognize that the calculated XMCD spectrum not only reproduces the observed fundamental structures A-E but also the shoulder F as shown in Figs.5 (c) and (d). It should be remarked here that a little bit larger $10Dq(=1.08)eV$ value compared to that for $\delta=0.11$ and 0.17 ($10Dq=0.7$eV) introduced the shoulder F in the XMCD spectra for $\delta=0.25$ and 0.33. From this result, $n_d$ is found to be 4.2 and the calculated $m_{spin}$ and $m_{orb}$ are estimated to be 3.2$\mu_B$ and -0.03$\mu_B$, respectively as listed in Table II. We find again that the small $m_{orb}$ is consistent with the XMCD result. The present $n_d$ and $m_{spin}$ are smaller than that for $\delta=0.11$ and 0.17. It is noted that the value of $m_{spin}$ is comparable to that obtained by the band structure calculation ($\sim3.3$ for both $\delta=0.25$ and 0.33\(^{18}\)), but is larger than the saturation magnetic moment of $\sim2.0-2.7\mu_B$.

Finally the calculated results for Cr$_3$S$_6$ are shown here. We have evaluated the value $V_{eq}=1.5$eV ($|pd\sigma|=0.87$eV) using the same formula as used for the telluride. It can be understood that the larger value for the sulfide is due to the reduced Cr-X atomic distance, where Cr-S and Cr-Te atomic distances evaluated by the X-ray powder diffraction are 2.4Å and 2.8Å, respectively. We have adjusted the parameters so as to fit the observed spectral features as shown in Fig.6. The obtained parameters are $\Delta=0.5$eV, $U_{dd}=3.1$eV and $10Dq=1.0$eV. The value of $U_{dd}=3.1$eV is consistent with the recent photoemission and inverse photoemission experiment by Koyama et al., where the energy splitting between the photoemission and inverse photoemission spectra is $\sim3.0$eV\(^{39}\). It is noticed that the XMCD spectrum of Cr$_3$S$_6$ in the ferrimagnetic phase has been reproduced with the same parameter set as shown in the inset of Fig.6, where the observed plus-minus feature is recognized in the calculation. The obtained positive $\Delta$ value for Cr$_3$S$_6$ is reasonable instead of the negative $\Delta$ for Cr$_{1-x}$Te because of the larger electron negativity of S than Te, which would be further confirmed by the reported larger value of $\Delta=5.2$eV for Cr$_2$O$_3$\(^{40}\). In Cr$_3$S$_6$, the $d^3$ and $d^5L^2$ states dominate the ground state, in contrast to the tellurides. The evaluated average electron number $n_d$ is found to be 3.8, which is smaller than that of the telluride with the same stoichiometry.
We have obtained the similar parameter values of Δ and 10Dq for Cr1−δTe with δ=0.11-0.33, which indicates that the local Cr 3d electronic states are not much affected by the Cr deficiency δ. This feature is really explained by the obtained negative value of Δ, where the lowest energy state can be described as dδL. 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 Cr1−δTe. This is consistent with the calculated band structure of Cr1−δTe, 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. In contrast, the positive Δ value for Cr5S6 leads to the lowest energy state of d1, which means the doped holes are likely to be in the Cr 3d orbitals. This interpretation is consistent with the ferrimagnetic resonance experiment on Cr5S6, where the electron hopping between the Cr2+ and Cr3+ ions is suggested.

V. CONCLUSION

We have observed the Cr 2p XAS and XMCD spectra of Cr8Te9 (δ=0.11), Cr5Te6 (δ=0.17), Cr3Te4 (δ=0.25), Cr2Te3 (δ=0.33) and Cr5S6. The observed changes with the Cr vacancy in the experimental XMCD spectra of Cr1−δTe are found to be small. The experimental XAS and XMCD spectra of Cr1−δTe have been compared with the result of the CI cluster-model calculation. We have obtained the best-fit parameter values, Δ=-2.0eV, 10Dq=0.7eV for δ=0.11 and 0.17 and Δ=-1.5eV and 10Dq=1.0eV for δ=0.25 and 0.33 with Udd=2.3eV and Vdd=1.3eV fixed for all of Cr1−δTe studied. Both the experiment and the calculation give a quenched Cr 3d orbital magnetic moment for Cr1−δTe, in agreement with the observed g value. The obtained values of the spin magnetic moment by the cluster model analyses are consistent with the results of the band structure calculation. In contrast to these negative Δ values for the tellurides, we have found the positive Δ (=0.5eV) for Cr5S6. It is concluded from these results that the doped holes created by the Cr deficiency exist mainly in the Te 5p orbitals for Cr1−δTe, whereas the holes are likely to be in Cr 3d state for Cr5S6. This interpretation for Cr1−δTe is consistent with the unchanged feature of the XMCD spectrum with the Cr defect concentration δ and the band structure calculation.

Acknowledgments

The authors would like to thank Dr. Y. Saitoh of the Japan Atomic Energy Research Institute for a fine adjustment of the monochromator and Professor A. Fujimori of the University of Tokyo and Professor T. Kanomata of Tohoku Gakuin University for their fruitful discussion. This work was done under the approval of the SPring-8 Advisory Committee (Proposal No. 2000B0439-NS-np). This work was supported by the Ministry of Education, Science, Sports and Culture.

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