Evidences for the Formation of Chromium in the Unusual Oxidation State Cr(IV)

III. Experimental Electronic Structure of the Channel Compounds Tl$_x$Cr$_5$Se$_8$ (*x* = 1 and 0.2)

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The X-ray photoemission core level spectra of TlCr$_5$Se$_8$ and Tl$_{0.2}$Cr$_5$Se$_8$ definitely exclude the oxidation of Tl(I) to Tl(III) when Tl is removed using a topotactic redox reaction between TlCr$_5$Se$_8$ and bromine in acetonitrile. Alterations are only observed for the multiplett structure of the Cr 3*s* core level giving evidences for a partial oxidation of Cr(III) to Cr(IV). Significant differences are observed in the valence band regions that were investigated with He I and He II radiation. For the Tl-poor sample an increased electron density at the Fermi level is observed in accordance with the higher electrical conductivity of this sample. The variations of the emissions in the region down to about 3 eV below E_F can nicely be explained on the basis of the reduced Tl content and a partial oxidation of Cr(III) to Cr(IV).

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INTRODUCTION

In the previous two contributions we investigated the fundamental question whether the guest atom Tl or host lattice [Cr$_5$Se$_8$] is oxidized during the topotactic redox reaction between bromine in acetonitrile using X-ray diffraction techniques as well as magnetic susceptibility measurements (1, 2). We demonstrated that the deintercalation of Tl from the ternary channel compound Tl$_x$Cr$_5$Se$_8$ ($0 \leq x \leq 1$) significantly influences the crystal structure as well as the magnetic properties. With decreasing Tl content mainly the interatomic Cr–Cr distances are altered whereas the (Cr/Tl)-Se bond lengths exhibit only minor changes. The minor changes of the Tl-Se bond lengths within the composition range definitely exclude the possibility of an oxidation of Tl(I) to Tl(III). But a final decision whether Cr(III) is oxidized to Cr(IV) or some of Se(-II) is oxidized to Se(-I), i.e.,

the formation of valence band holes, could not be drawn from the room temperature experiments.

Low-temperature X-ray experiments performed on selected single crystals showed an unusual unit cell volume expansion at about 125 K. The alterations of the Cr–Cr distances at room temperature as a function of x and the changes observed upon cooling let us conclude that part of the Cr(III) is oxidized to Cr(IV). We further gave evidences that the positive charge is trapped on one of the three possible crystallographic Cr sites. These conclusions were supported by the magnetic susceptibility measurements. Whereas the stoichiometric compound is a simple three-dimensional antiferromagnet with $T_N = 55$ K, the Tl-poor samples exhibit a complex magnetic behavior. For all samples with $x < 1$ the susceptibility passes a maximum at $T_{max} \approx 125$ K and steeply drops to a value comparable to that obtained at room temperature. To get an impression of the highly different magnetical behavior the susceptibility curves for TlCr$_5$Se$_8$ and Tl$_{0.2}$Cr$_5$Se$_8$ are shown in Fig. 1.

The height of the susceptibility maximum strongly depends on the Tl content. With decreasing Tl content the effective magnetic moment decreases reaching the theoretical spin only value for a mixed Cr(III) d^3 and Cr(IV) d^2 spin system at $x \approx 0$. Above $x = 0.5$ the predominant exchange is antiferromagnetic and below this value it is ferromagnetic. This highly unusual behavior of the Tl-poor samples was qualitatively explained on the basis of the formation of Cr(III) and Cr(IV). At room temperature the additional hole is mobile moving between different Cr atoms. Upon cooling the hole is trapped eventually on site Cr2 giving rise to a significant expansion of the Cr2–Cr2 distance, of the crystallogrphic b axis, and of the unit cell volume at 125 K.
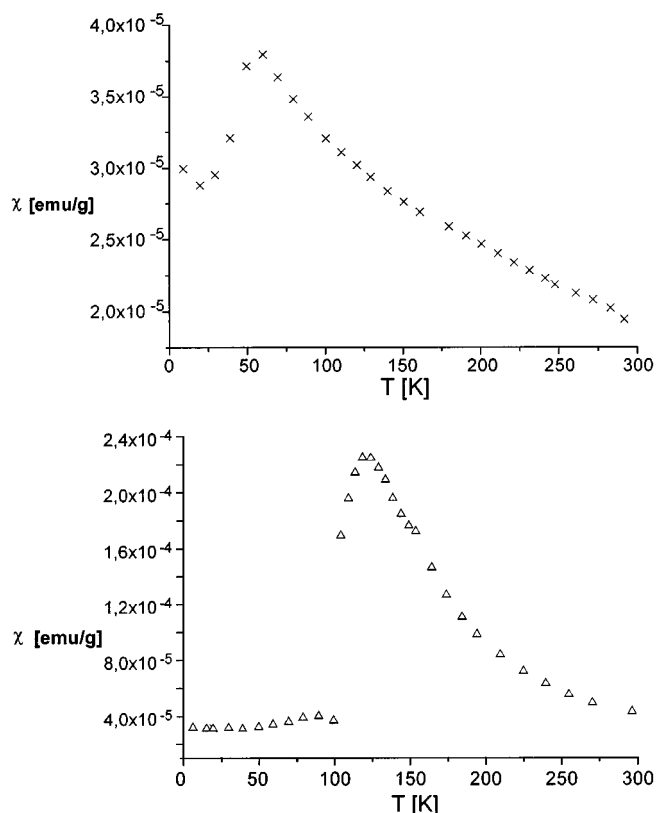
FIG. 1. The temperature dependence of the magnetic susceptibilities of $TlCr_5Se_8$ (top) and $Tl_{0.2}Cr_5Se_8$ (bottom). Note the different scaling of the y axis and the highly different temperature dependence of χ.

The possibility of the formation of valence band holes, i.e., the partial oxidation of Se(-II), was excluded.

Recently we investigated the ternary channel compound $Tl_xCr_3S_5$ (3) with X-ray photoemission (XPS) and He I/He II ultraviolet photoemission (UPS). The detailed analysis of the valence band spectra and the core level regions gave evidences for the formation of valence band holes, in accordance with what is expected from the energy of the sulfur sp band that destabilizes Cr^{4+} (4). Whereas changes of the valence band spectra were associated with alterations of the Tl content and of the Cr–Cr/Cr–S bonding interactions no differences were observed for the Cr $2p$ and Cr $3s$ as well as Tl $4f$ core levels. But pronounced differences were found for the S $2p$ core level that exhibits a drastic increase in the full width at half maximum when x in $Tl_xCr_3S_5$ is reduced from 1 to 0.5. Such a broadening can be attributed to the formation of S(-I).

The present contribution presents the results of XPS and UPS investigations performed on the two samples $TlCr_5Se_8$ and $Tl_{0.2}Cr_5Se_8$. The XPS investigations are a hard challenge because if one Cr(III) is oxidized to Cr(IV) only one electron is removed from the 5 Cr centers, i.e., a change of 0.2 electrons per Cr. The situation becomes more difficult if

one Se(II) is oxidized to Se(-I). In this case the removal of one electron is *compensated* by 8 Se centers; i.e., the charge on the Se alters by only 0.125 electrons per Se. On the other hand the valence band region consisting of Cr $3d$, Se $4p$ as well as of Tl $6s$ and $6p$ states should reflect the changes introduced by the removal of Tl.

EXPERIMENTAL

The preparation of stoichiometric $TlCr_5Se_8$ as well as of the Tl-poor samples was described elsewhere (1, 2). Tl-poor samples were obtained via a topotactic redox reaction using bromine in acetonitrile as oxidizing agent. The homogeneity of the samples was checked with X-ray powder diffractometry (STOE STADI P diffractometer, monochromized $CuK\alpha$, $\lambda = 1.54056$ Å).

X-ray photoelectron spectroscopy (XPS, $MgK\alpha = 1253.6$ eV) and ultraviolet photoelectron spectroscopy (UPS, He I = 21.2 eV, He II = 40.8 eV) were carried out in a Leybold LHS 12 MCD system equipped with an EA 200 analyzer. The base pressure of the apparatus was 2×10^{-10} Torr. The energy scale was calibrated using Au $4f_{7/2} = 84.0$ eV. The quantitative results were obtained after Shirley background subtraction and integration using the empirically derived cross sections of (5). The $Tl_xCr_5Se_8$ samples were transferred into the preparation chamber (base pressure 1×10^{-9} mbar) as loose powders in a mortar-like stainless steel sample holder. A wobble stick (VG Instruments) equipped with a stainless steel pestle was used to grind the samples in UHV.

RESULTS AND DISCUSSION

1. The Core Level Regions of Tl, Cr, and Se

As noted in the Introduction, the redox reaction is accompanied by a minute change in the electron density located on the different atoms in the host lattice. But to further support our conclusions drawn from the X-ray scattering experiments that Tl^+ is not oxidized to Tl^{3+} the Tl $4f_{5/2}$ and $4f_{7/2}$ core level lines were measured (see Fig. 2). The line shape of the Tl $4f$ core level is different from a purely metallic system as a consequence of the different core hole coupling in the systems $Tl_xCr_5S_8$ without delocalized valence electrons and thallium metal with delocalized valence electrons. The b.e.s for the $4f_{5/2}$ and $4f_{7/2}$ core levels are 122.9 and 118.4 eV for both samples with a spin-orbit coupling of 4.6 eV being nearly identical to the values obtained for $Tl_xCr_3S_5$ (3), TlV_5S_8 (8), $TlCr_5S_8$ (9), Tl_2S, $TlSbS_2$, and $TlSb_3S_5$ (10), but lower than the values observed for ternary compounds such as Tl_3NbS_4 and Tl_3VS_4. The latter compounds are, however, structurally different and contain isolated Tl ions located between MS_4 tetrahedra.

A comparison with more ionic compounds like TlF suggests that the Tl atoms carry only a small positive charge.
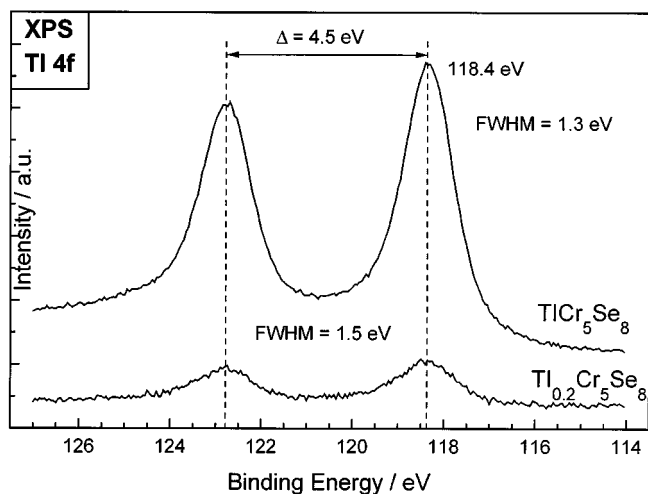
FIG. 2. The XPS Tl $4f$ core level regions of TlCr$_5$Se$_8$ and Tl$_{0.2}$Cr$_5$Se$_8$.

The FWHM of about 1.3 eV for the stoichiometric sample and 1.5 eV for the Tl-poor compound are comparable with the FWHM of elemental Tl (11). Both the unchanged peak shape and the absence of a shift to a higher b.e. due to deintercalation indicate that the valence state of Tl is identical in TlCr$_5$Se$_8$ and the Tl-poor sample. These results further highly suggest that during the chemical redox reaction Tl is not oxidized from Tl(I) to Tl(III). This is in line with the results obtained on selected single crystals using X-ray crystallography that definitely let us exclude the formation of a Tl(III) species (1).

The Se $3d$ and Cr $2p$ core level regions show no differences between the stoichiometric and Tl-poor sample. The overall features as well as binding energies are identical to our previously published data for TlCr$_5$Se$_8$ (12).

The Cr $3s$ core level spectra of TlCr$_5$Se$_8$ and of the Tl-deintercalated sample are displayed in Fig. 3. The multiplet splitting is clearly observable: the Cr $3s$ state is split by exchange interaction in two peaks located at 73.6 and 76.8 eV for TlCr$_5$Se$_8$ and at 74.0 and 77.3 eV for Tl$_{0.2}$Cr$_5$Se$_8$. The higher b.e. observed for Tl$_{0.2}$Cr$_5$Se$_8$ is an indication of a slightly larger positive charge located on the Cr atoms.

By ejecting a Cr $3s$ photoelectron, two final states are possible: $3s \, 3d^3 \, {}^3F$ ($S = 1$, $L = 3$) or $3s \, 3d^3 \, {}^5F$ ($S = 2$, $L = 3$). The main difference between these final-state configurations is that in the former state the spins of the remaining $3s$ electron are coupled antiparallel to those of the $3d$ electrons, whereas in the latter state the spins of the $3s$ and $3d$ electrons are coupled parallel. The ^5F state is energetically lowered due to the favored parallel spin exchange interaction. The magnitude of the energy separation is proportional to the $3s$–$3d$ exchange integral. In the simplest model, the intensity ratio is approximately governed by the mul-

tiplet ratio, i.e., 5:3. For TlCr$_5$Se$_8$, the intensity ratio seems to be higher than that for Tl$_{0.2}$Cr$_5$Se$_8$, providing further evidence for significant changes in the electronic configuration of the Cr atoms when Tl is removed from TlCr$_5$Se$_8$. In more ionic compounds such as CrCl$_3$, a multiplet splitting of about 4.5 eV was reported with the main peak at 75 eV and the satellite at 79.5 eV (13). The magnitude of the energy separation and the mean b.e. depend on the bonding properties of the solid; i.e., they are a function of covalency as shown by Clark and Adams (14) for complexes of Cr with different oxidation states and ligands.

2. The He I and He II Valence Band Spectra

The He I and He II valence band spectra for TlCr$_5$Se$_8$ and Tl$_{0.2}$Cr$_5$Se$_8$ are displayed in Figs. 4 and 5. For both samples the intensity of the emission at the emission threshold is low, suggesting that both samples are poor metals or semiconductors. A closer inspection of the valence band spectra at $E_F = 0$ eV reveals that the removal of Tl from TlCr$_5$Se$_8$ leads to an increased electron density at the Fermi level. This observation implies that Tl$_{0.2}$Cr$_5$Se$_8$ should have a higher electrical conductivity than TlCr$_5$Se$_8$. Preliminary resistivity measurements performed on pressed powder

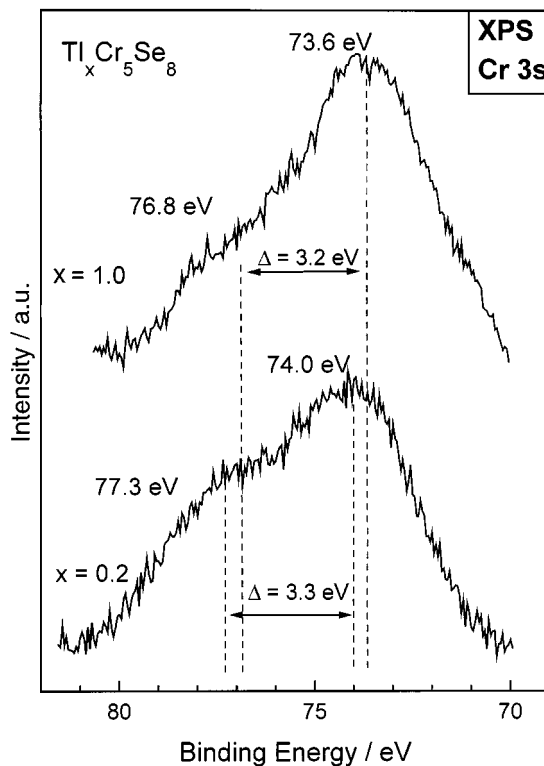**FIG. 3.** The XPS Cr $3s$ core level regions of TlCr$_5$Se$_8$ and Tl$_{0.2}$Cr$_5$Se$_8$. The binding energies for the main peaks and for the satellites as well as the multiplet splittings Δ are given.

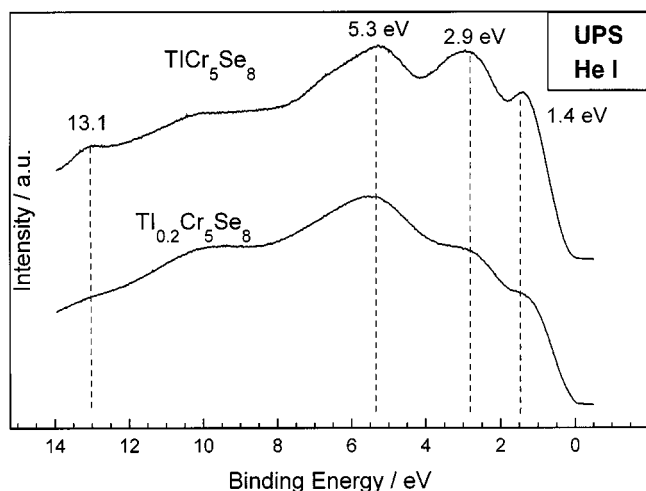**FIG. 4.** The He I valence band spectra of $TlCr_5Se_8$ and $Tl_{0.2}Cr_5Se_8$. The numbers are the binding energies of the most prominent emissions.

pellets of $TlCr_5Se_8$ and $Tl_{0.2}Cr_5Se_8$ show a higher conductivity of the Tl-poor sample by a factor of about 10.

The normalized shallow Tl $5d_{3/2}$ and $5d_{5/2}$ core level lines are displayed in more detail in the inset of Fig. 5. The shape, spin-orbit coupling (2.2 eV), and FWHM are identical for both samples. The b.e. for the Tl $5d_{5/2}$ peak amounts to 13.1 eV for $TlCr_5Se_8$ and slightly shifts to a lower value for the Tl-poor sample. The b.e.s are somewhat lower than those found for the other ternary thallium chalcogenides mentioned above.

Below the Fermi level three well-resolved peaks can be distinguished at about 1.4, 2.9, and 5.3 eV. The height of the
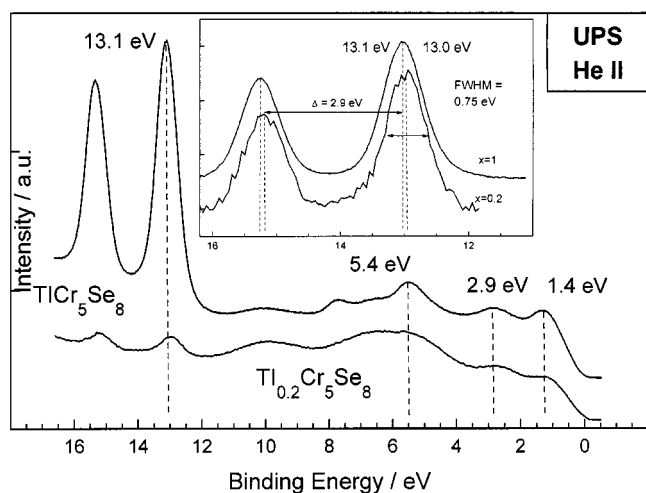

FIG. 5. The He II valence band spectra of $TlCr_5Se_8$ and $Tl_{0.2}Cr_5Se_8$. The numbers are the binding energies of the most prominent emissions. The inset shows an enlarged view of the Tl $5d$ shallow core level region. Note that the Tl $5d$ spectrum of $Tl_{0.2}Cr_5Se_8$ was rescaled.

peaks at 1.4 and 2.9 eV below E_F seem to be more pronounced in the Tl-rich sample, whereas the emission at 5.3 eV shows no significant variation with Tl content. Using the empirical cross sections for Se, Cr, and Tl tabulated in Refs. (5) and (6), the different peaks can be assigned to Se $4p$ states (5.3 eV), Cr $3d$ states (3 and 1.4 eV), and Tl $6s$ states (1.4 eV). A localized Cr $3d^2$ hole state at 3 eV below E_F is found in Cr_2O_3 (15) and $CrCl_3$ (13). The assignment of the emission at 1.4 eV below the emission threshold is supported by UPS investigations of the series $TlV_{5-y}Cr_yS_8$ (7). With increasing Cr content a peak became more clearly resolved at about 1.2 eV below E_F and grew in intensity with increasing Cr concentration.

The change of the intensities of the peaks at 1.4 and 2.9 eV as a function of Tl content can be deduced directly from the normalized valence band spectra shown in Fig. 6. A significant reduction is observed for the emission at 1.4 eV relative to the intensity of the peak at 2.9 eV. Because during the redox reaction Tl is removed from $TlCr_5Se_8$ the change in the intensity might be mainly due to reduced Tl contributions. This conclusion would be in agreement with the results of photoemission experiments performed on $Tl_xCr_3S_5$ samples (3) that showed a decrease in the intensity of the peak at 1.4 eV below E_F with decreasing Tl content. A rough estimate of the intensity drop of the emission at 1.4 eV when the Tl content is lowered from 1 to 0.2 leads to about 10 and 20% for He I and He II, respectively. However, the cross
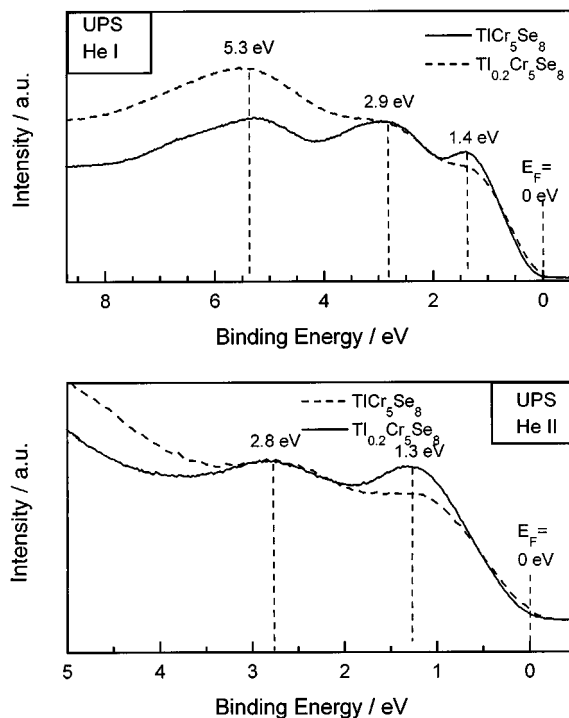

FIG. 6. The normalized He I (top) and He II (bottom) valence band spectra of $TlCr_5Se_8$ and $Tl_{0.2}Cr_5Se_8$.

sections for Cr 3d are 9.230 (He I) and 8.540 (He II), and for the Tl 6s/p levels the values are 0.043/0.4181 (He I) and 0.1163/0.063 (He II) (6). If Cr 3d as well as Tl 6s/p contribute to the emission at 1.4 eV, the fraction of the Tl levels to the intensity is about 5% for He I and 2% for He II. For a Tl-free sample one would expect a decrease in the intensity of the same order. On the other hand, the lowering of the electron density located on the Cr atoms should have a more pronounced effect due to the significantly larger cross sections. A coarse approximation assumes that the intensity should be reduced by about 7% if one Cr(III) d^3 atom is oxidized to Cr(IV) d^2. The sum of both contributions gives the correct trend, i.e., a reduction of the intensity of the peak at 1.4 eV of about 10%. But one must keep in mind that the removal of Tl also introduces significant changes in the interatomic bonding interactions (1), and some of the observed changes in the spectra are also caused by these alterations.

CONCLUSIONS

The photoemission experiments clearly show that the topotactical removal of Tl atoms from TlCr$_5$Se$_8$ does not result in an oxidation of the electropositive Tl(I) to Tl(III). The core level spectra except the Cr 3s spectra show no significant differences between the two samples. This result is not surprising because the removal of one electron out of five Cr(III) centers leads to a reduction in the average oxidation number to 2.8 (a change of only 0.2 units per Cr atom being too little to be detectable with the spectrometer used). But the detailed analysis of the UP valence band spectra provides evidence for noticeable changes within the Cr$_5$Se$_8$ host lattice. A significant drop in the intensity of an emission at 1.3 eV can only be explained on the basis of reduced contributions from Tl 6s/p and Cr 3d states.

To this end, it seems to be necessary to discuss the possible formation of Cr(IV) within a selenide matrix in more detail. It is highly interesting that very recently Hibble et al. (16) published results of EXAFS studies as well as magnetic susceptibility measurements of CrS$_3$ and CrSe$_3$. They formulated CrS$_3$ as Cr^{III}(S$_2^{-I}$)$_{1.5}$ and CrSe$_3$ as Cr^{IV}(Se$_2^{-I}$)Se^{-II}, and they noted that the more weakly oxidizing chalcogen Se gives the chromium compound with Cr in the higher formal oxidation state. But both the EXAFS results and the effective magnetic moment per Cr undoubtly support these formulations. The existence of appreciable amounts of Cr(IV) was also postulated for CrSe$_2$, which was obtained by a topotactic redox reaction between K$_x$CrSe$_2$ and iodine in acetonitrile (17). On the other hand Schöllhorn et al. presented evidences that in chalcogen spinels CuCr$_2$X$_4$ (X = S, Se, Te) anion p band holes exist leading to the formulation Cu^I(Cr^{III})$_2$(X^{-I})(X^{-II})$_3$ (18–20). As mentioned in the Introduction valence band hole formation was postulated for Tl$_x$Cr$_3$S$_5$ (3).

These contradicting results suggest that the actual crystal structure and therefore the resulting electronic band structure determine whether the oxidation takes place in the cationic or anionic sublattice. To shed light on this problem we started to calculate the electronic band structure of TlCr$_5$Se$_8$ (21). A preliminary density of states (DOS) curve is shown in Fig. 7 and our results can be summarized as follows. The DOS at E_F is very low, supporting the observations of the experimental He I and He II UP spectra. Just below E_F a sharp band is found that is dominated by Cr 3d states with a low contribution of Se 4p states reflecting the covalent nature of the Cr–Se bonds. Between about 1.5 and 4 eV below E_F the valence band is dominated by Se p states. From this DOS curve it is clear that during an oxidation reaction Cr 3d electronic density is removed leading to the formation of Cr(IV). In addition, the removal of electronic density shifts the E_F into the tail of the Cr 3d dominated band, thus leading to a higher DOS at E_F. It must be noted that for the Tl-deintercalated sample an increased electron density at the Fermi level was found in the experimental He I and He II UP spectra.

A highly interesting behavior was reported for the Li/TiS$_2$ system, which may serve as a model to explain why the Se p band is not higher in energy than the Cr 3d band. The sulfur sp band of the pristine material TiS$_2$ was pushed down by about 1 eV after intercalation of one Li leading to LiTiS$_2$ (22). A binary Cr$_5$Se$_8$ with the TlCr$_5$Se$_8$ structure type is not known, but the ternary compound ACr$_5$Se$_8$ can be obtained using a high-temperature annealing technique. If such a shift in the Se p band is mediated by the intercalated A^{n+} cations the chemical behavior as well as the formation of Cr(IV) can be rationalized.
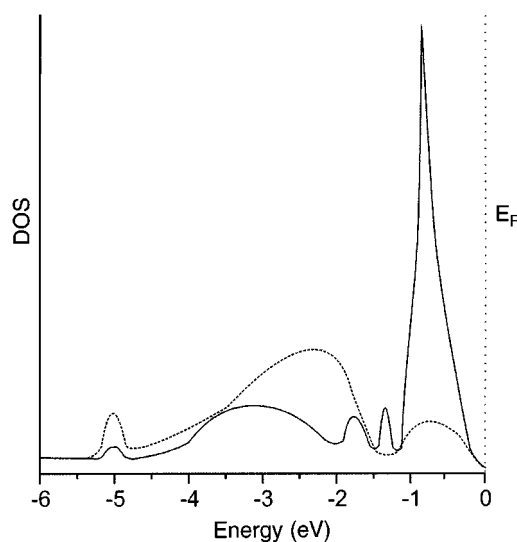

FIG. 7. Density of states (DOS) curve for TlCr$_5$Se$_8$. Dotted line, Se contribution; continuous line, Cr contribution. The contribution of Tl states is very low and is omitted for clarity.

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