

# Electronic structure of molecular superconductors containing paramagnetic 3d ions

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## INTRODUCTION

The charge transfer salts based on the donor ET-molecule [bis (ethylenedithio) tetrathiafulvalene] display a wide range of properties from highly conducting metallic to superconducting to wide band gap semiconducting and insulating [1]. Typically the crystal structure of such compounds is characterized by the spatial segregation of organic cations and inorganic anions into alternating layers, often referred to chemically constructed multilayers.

Among the many ET-based charge transfer salts, new molecular conductors and superconductors containing paramagnetic Fe<sup>III</sup> and Cr<sup>III</sup> ions have been synthesized recently such as: (ET)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CN (T<sub>c</sub>=8.5 K) [Ref. 2], (ET)<sub>4</sub>[(H<sub>3</sub>O)Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CN (T<sub>c</sub>~6 K) [Ref. 3] and (ET)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>5</sub>H<sub>5</sub>N [Ref. 4]. These were the first superconducting phases containing stoichiometric concentrations of paramagnetic 3d ions to be reported.

The crystal structure of these compounds consists of ET-layers with +0.5 formal charge per molecule and layers containing H<sub>3</sub>O<sup>+</sup> and [Me(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> (Me=Cr, Fe). The solvent molecules occupy hexagonal cavities formed by the anionic layer. A most intriguing feature is that the change of the solvent molecule C<sub>6</sub>H<sub>5</sub>CN (benzonitrile) to C<sub>5</sub>H<sub>5</sub>N (pyridine) induces a dramatic change in the observed physical properties: (ET)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CN shows a metal-superconductor transition at 8.5 K whereas (ET)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>5</sub>H<sub>5</sub>N exhibits a metal-insulator transition at 116 K [2, 4]. It is therefore of great interest to examine the electronic structure of these compounds more closely. We present results of X-ray fluorescence measurements of (ET)<sub>4</sub>[(H<sub>3</sub>O)Me(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CN (Me=Cr, Fe) and (ET)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>5</sub>H<sub>5</sub>N. The C K $\alpha$ , N K $\alpha$  (2p $\rightarrow$ 1s transition) and Me L<sub>2,3</sub> (3d<sub>4s</sub> $\rightarrow$ 2p<sub>3/2,1/2</sub> transition) (with Me=Fe, Cr) X-ray emission spectra probe the occupied C 2p, N 2p, Cr 3d<sub>4s</sub> and Fe 3d<sub>4s</sub> density of states located within or close to the valence band.

## EXPERIMENTAL

Single crystals of (ET)<sub>4</sub>[(H<sub>3</sub>O)Me(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CN (Me=Cr, Fe) and (ET)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>5</sub>H<sub>5</sub>N were grown by electrocrystallization in H-shaped cells as previously reported [2, 3, 4]. The single crystals of (ET)<sub>4</sub>Hg<sub>2.89</sub>Br<sub>8</sub> were synthesized by

electrochemical oxidation of ET under constant current of 0.5  $\mu\text{A}$  at 40 $^\circ\text{C}$  from a solution containing  $2 \cdot 10^{-3}$  M BEDT-TTF,  $1.5 \cdot 10^{-2}$  M  $\text{Bu}_4\text{NHgBr}_3$ ,  $10^{-3}$  trichlorethane, and  $10^{-3}$  M  $\text{HgBr}_2$ .

The carbon and nitrogen  $\text{K}\alpha$  ( $2\text{p} \rightarrow 1\text{s}$  transition) and  $\text{Me L}_{2,3}$  ( $3\text{d}4\text{s} \rightarrow 2\text{p}_{3/2,1/2}$  transition) ( $\text{Me}=\text{Cr}, \text{Fe}$ ) spectra were recorded at the Advanced Light Source (Beamline 8.0) using the soft X-ray fluorescence endstation. The carbon and nitrogen  $\text{K}\alpha$  spectra were obtained with an energy resolution of about 0.8 eV. All XES spectra presented in this paper were measured at a temperature of  $T=70^\circ\text{K}$  in order to reduce decomposition of the organic compounds during the exposure.

## RESULTS AND DISCUSSION

Figure 1 shows the Fe  $\text{L}_{2,3}$  X-ray emission spectrum of the oxalate anionic layer of  $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ . For comparison, the Fe  $\text{L}_{2,3}$  X-ray emission spectra of Fe-metal, FeO and  $\text{Fe}_2\text{O}_3$  are also shown. It is known that the ratio of intensities at the  $\text{L}_2$  ( $3\text{d}4\text{s} \rightarrow \text{p}_{1/2}$  transition) threshold to  $\text{L}_3$  ( $3\text{d}4\text{s} \rightarrow 2\text{p}_{3/2}$  transition) threshold differs from the value of 1/2 and reflects the occupancy of  $\text{L}_2$  and  $\text{L}_3$  levels and therefore depends on the chemical state of the elements. For the spectra of 3d metals and alloys, the ratio  $I(\text{L}_2)/I(\text{L}_3)$  is very small due to the Coster-Kronig process

$\text{L}_2\text{L}_3\text{M}_{4,5}$ . The probability of non-radiative  $\text{L}_2\text{L}_3\text{M}_{4,5}$  Coster-Kronig transitions is distinctly lower for 3d oxides than for metals due to the presence of an energy gap. The  $I(\text{L}_2)/I(\text{L}_3)$  intensity ratio should increase going from pure metals to metal oxides [5]. Moreover, the  $I(\text{L}_2)/I(\text{L}_3)$  ratio decreases in the sequence  $\text{MnO} - \text{Mn}_2\text{O}_3 - \text{MnO}_2$  [6]. For  $\text{MnO}$ , with the maximum number of unpaired 3d electrons, the intensity of the  $\text{Mn L}_2$  line is nearly equal to that of the  $\text{Mn L}_3$  line, but increasing covalency leads to reduction of this ratio. Therefore, the  $I(\text{MeL}_2)/I(\text{MeL}_3)$  ratio is related to the localization of the 3d electrons and hence the magnetic moment because the exchange interaction energy of the 3d electrons exceeds the spin-orbit interaction energy at least by one order of magnitude. This favors a substantial decrease in the statistical weight of the  $3\text{d} \rightarrow 2\text{p}_{3/2}$  transition.

In Fig. 2, the Cr  $\text{L}_{2,3}$  X-ray emission spectra of  $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ , the Cr-metal and  $\text{LiCrO}_2$  are shown. In  $\text{LiCrO}_2$ , Cr ions have the electronic configuration  $3\text{d}^3$  [6]. The Cr  $\text{L}_{2,3}$  spectrum of  $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$  shows a shoulder at 570 eV, like that seen in the sample of  $\text{LiCrO}_2$ , which corresponds to the hybridization between Cr 3d and O 2p states.

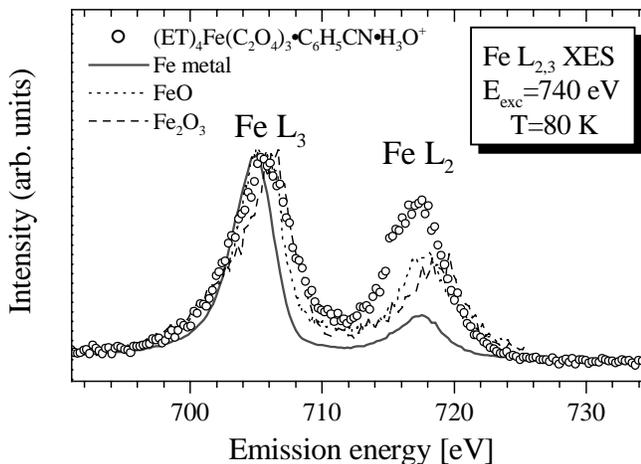


Fig.1 The Fe  $\text{L}_{2,3}$  emission spectra of  $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ,  $\text{Fe}_2\text{O}_3$ , FeO, and Fe-metal.

According to Figures 1 and 2, the intensity ratio  $I(\text{MeL}_2)/I(\text{MeL}_3)$  for the samples

$(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$  and  $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$  is almost three times higher than in the pure metals (Fe and Cr) and two times higher than in  $\text{Fe}_2\text{O}_3$  and  $\text{LiCrO}_2$ , respectively. We attribute such large enhancement in this ratio to the highly ionic and insulating character of the oxalate layers and to the localization of the 3d electrons. The local magnetic moments at 3d metal sites are found to be very high: 5.92 and 3.96  $\mu_B$  for  $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$  and  $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ , respectively.

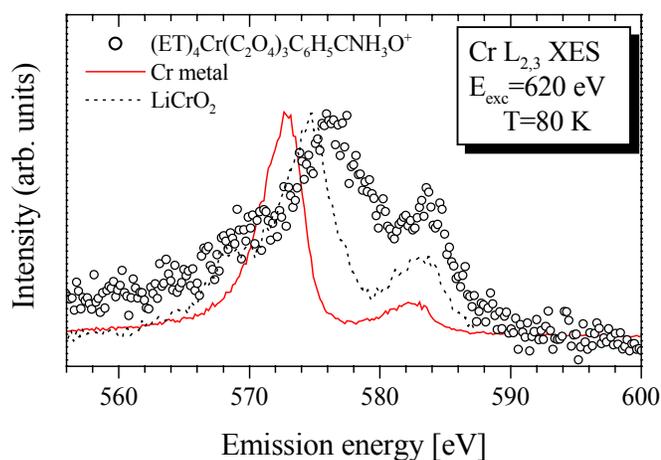


Fig.2 The Cr  $L_{2,3}$  emission spectra of  $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ ,  $\text{LiCrO}_2$ , and Cr-metal.

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