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Juana Acrivos
San José State University

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XANES in $(TMTSeF)_2ReO_4$: Polarisation Dependence of the Se K edge

S.S.P. Parkin
IBM Research K32/281, 5600 Cottle Road, San José, CA 95193
and
J. V. Acrivos
San Jose State University, San Jose, CA 95912

Résumé — Nous avons mésuré les spectres d'absorption de rayons X près de profils de raies du rhénium L_i (i=I,II,III) dans $(TMTTF)_2ReO_4$ et $(TMTSeF)_2ReO_4$ et la raie de Se K dans le dernier composé. La structure du spectre d'absorption de la raie Se K dépend beaucoup de la polarisation du rayon incident par rapport aux axes du crystal: son interprètation peut donner des informations sur la symmétrie des états non occupés de la bande de conduction. On compare les positions du bord de la raie de rhénium avec celles de plusieurs composés inorganiques contenant du rhénium dans différentes états d'oxidation, et on trouve les mêmes positions, aux erreurs experimentales près, que celles , obtenues dans $KReO_4$. Ceci suggère que l'environnement moléculaire dans les matériaux organiques affecte peu l'état chimique de l'anion perrhenate.

Abstract— We have measured XANES (X-ray Absorption Near Edge Spectra) near the Re L*i* (i=I,II,III) edges in $(TMTTF)_2ReO_4$ and $(TMTSeF)_2ReO_4$ and the Se K edge in the latter compound. An important dependence of the XANES at the Se K edge on the polarisation of the incident beam with respect to the crystal axes was observed, whose interpretation can give information on the symmetry of the unoccupied conduction band states. The positions of the Re L edges were compared with those in several inorganic compounds containing Re in various oxidation states, and were found to be, within experimental error, the same as those in $KReO_4$, suggesting the molecular environment in the organic materials affects little the chemical state of the perrhenate anion.

I: Introduction

In this paper we present x-ray absorption measurements of the Re L edges and the Se K edge in $(TMTSeF)_2ReO_4$. The motivation of these studies was two-fold; firstly to examine the valence state and environment of the Re atom and secondly to learn something about the nature of the conduction band states by considering various Se and Re edge XAS. X-ray Absorption spectroscopy (XAS) can give useful information concerning the chemical state of the absorbing element from the position of the absorption edge. For metals, the density of states and details of the symmetry of the unoccupied conduction band states can be deduced from structure in the pre-edge region, the X-ray Absorption Near Edge Structure (XANES) /1,2/, originally termed "white lines", by Cauchois and Mott /3,4/. White lines have been observed at the L and K edges of many transition metals /1,2,5,6/. However the XANES is complicated by many-body effects, involving for example, final state interactions with the core hole (exciton effects), screened out to some extent in a metal, with the possibility of formation of induced bound states /7,8/. The spectra thus generally give information about the final excited states of the system, making comparison with theory more difficult, although the initial state, by contrast, is well defined. Lifetime broadening means that the resolution of this experiment is poor (1-10 eV) compared to other techniques particularly in the hard x-ray region /9/. XANES has been applied to very few low dimensional metallic systems /10,11/: these studies are the first measurements on single crystals of organic linear chain conductors, allowing an examination, for the first time of the polarisation dependence of the x-ray spectra.

II: Results

Re L edge XAS

The XANES measurements were made at the Stanford Synchrotron Radiation Laboratory (SSRL) using standard procedures /1,2/ and the experimental configuration shown in figure 1. For these experiments the radiation was obtained from the SPEAR storage ring operating at 3 GeV and 25-70 mA. The single crystal samples were masked with lead tape and positioned within the incident beam by maximising the transmitted radiation near an absorption edge.

Figure 2 shows plots of transmittance $(\ln(I/I_0)$- see fig 1) versus energy near the Re L_I edge in $(TMTSeF)_2ReO_4$ and in various Re salts. (Bragg reflections of the transmitted x-ray beam from silicon wafers, as shown in figure 1, were used as energy reference markers for each scan /12/). Results were also obtained for other Re salts, so that the position of the L_I edge was determined for Re in various chemical states. As shown in figure 2 the L_I edge is shifted to higher energy by about 2.5 eV for a change in formal valence state of Re of +3, from +7 in $KReO_4$ to +4 in ReS_2. The position of the L_I edge in $(TMTSeF)_2ReO_4$ is, within experimental error (± 0.3 eV), the same as that in $KReO_4$, indicating that the Re in the organic metal has a chemical state similar to that in the inorganic salt. Moreover the EXAFS structure above the edge has a similar form in both the organic and inorganic perrhenate salts. This result shows that the ReO_4^- anion in $(TMTSeF)_2ReO_4$ has substantially the same structure as that in $KReO_4$, which means that the anion is not greatly modified by interactions with the cage in which it sits within the organic molecular structural framework: there is no indication of backbonding of the oxygen lone-pair orbitals with the closest Se atoms in the neighbouring TMTSeF molecules, which would affect the position of the Re edge through charge screening, even though structural studies suggest the possibility of such an O-Se bond /13/. These studies thus suggest the Re atom has a valence state close to that of Re in the inorganic salt. XANES measurements were also made for the isostructural sulphur analogue, $(TMTTF)_2ReO_4$ /14/, with similar results. The same conclusions were obtained from a comparison of the Re L_{II} and L_{III} edges in the organic compounds with those in the standards.

Se K edge XAS

The x-ray beam from a synchrotron is highly polarised along a direction, **E**, in the plane of the synchrotron, and perpendicular to the propagation vector, **k**. In these experiments the dependence of the XANES was considered as a function of the polarisation of the incident x-ray beam, by rotating the sample about the axes, ϕ and θ shown in figure 3. ϕ is normal to both **E** and **k**, and θ is along the normal to the plane of the sample, the crystallographic axis, c /13/. The long axis of the sample, a, was aligned parallel to **E** for $\phi=\theta=0$. Changing ϕ and θ had no effect on the XANES at the Re L edges, but an important dependence of the structure at the Se K edge on the polarisation of the x-ray beam was found. (Note that it was not possible to measure the S K edge in the TMTTF salt because of a low photon flux for energies close to this edge). XANES data are shown in figure 3 for several θ and ϕ. Close to $\phi=\theta=0$ three features in the edge region can be distinguished. There is a shoulder (FI) close to E=0 and two peaks at higher energies. The first peak (FII) exhibits a strong polarisation dependence: as θ is varied away from 0, at $\phi=0$, the intensity of this peak grows to reach a maximum at $\theta=90°$ (figure 3(a)). Varying ϕ with $\theta=90°$ has no effect on the XANES spectra (figure 3(b)). The strength of FII increases as ϕ is varied away from 0 with $\theta=0$. These results show that the strength of FII depends on the component of **E** along a with the largest value, for **E** perpendicular to a. Varying the direction of **E** within the transverse plane perpendicular to a has no effect on this feature. The third feature, FIII, is much weaker than FII and is most intense for **E** along a.

As mentioned above, structure within a few eV of the edge in a metal is believed to be associated with transitions from core states into partially occupied conduction band states. The strength of such structure will depend on the density of final states and the matrix element for the transition. The optical dipole selection rules will apply so that, for example, transitions from a K core state, will involve final states of predominantly p symmetry. Within such a framework FI may correspond to the Fermi energy. FII, which is within 3 eV of the edge, will result from transitions into unoccupied conduction band states, but FIII, at almost 10 eV above the edge probably involves many-body effects and is more difficult to classify. We consider further an interpretation of FII.

MO Interpretation of the XANES

At the origin of the Brillouin zone the orbitals transform within the point group symmetry of the isolated molecule, D_{2h} (assuming free rotation of the methyl groups). For one molecule the four

non-interacting Se 1s orbitals give rise to initial states of symmetry $[|i(\gamma)>] = [a_g, b_{1g}, b_{2u}, b_{3u}]$
Simple group theory shows that the transition matrix element $M_{if} = <f|eE|i>$ will be non-zero when the final state has the following symmetry (described by the irreducible representations of the D_{2h} group), depending on the initial state $|i>$ and the polarisation, E, (where we define z to be normal to the plane of the TMTSeF molecule, i.e. along a in the crystal).

$$|f> = \begin{array}{ccc|c} x & y & z & |i> \\ \hline \sigma & \sigma & \pi & \\ b_{3u} & b_{2u} & b_{1u} & a_g \\ b_{2u} & b_{3u} & a_u & b_{1g} \\ b_{1g} & a_g & b_{3g} & b_{2u} \\ a_{1g} & b_{1g} & b_{2g} & b_{3u} \end{array} \qquad (1)$$

The final states can be described as having π or σ symmetry according to whether or not the sign of the molecular orbital changes on reflection through the plane of the molecule. The transition strength also depends on the coefficient, $a\zeta(\gamma,n)$, of the Se $4p$ atomic orbitals in the final state MO, through the matrix element $|M_{if}|^2 = |a_\zeta(\gamma,n)|^2 |<1s|M_\zeta|4p_\zeta>|^2$ where $\zeta =x,y,z$ and the γ,n refer to the various MO. One may then deduce from the polarisation dependence of the strength of FI and FII the relative magnitudes of $|a_\zeta|^2$ for the different final states. The results in figure 3 indicate that $|a_z|^2 << |a_{x,y}|^2$. This means that most of the 4 p_z orbitals are filled in the conduction band so primarily excitations to the $4p_x$ and $4p_y$ orbitals are allowed. This is in agreement with calculations of the LUMO for the related molecule, TTF, which give a relative charge concentration at the Se atom of 1:4 for the π and σ orbitals /15/.
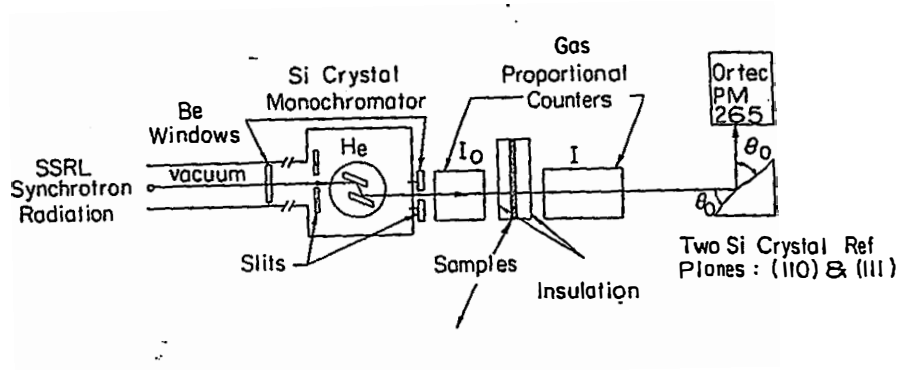
III: Conclusions

We have measured XANES at the Re L edges in $(TMTSeF)_2ReO_4$ and $(TMTTF)_2ReO_4$. No shift in position of the Re L edges with respect to those in $K ReO_4$ was found, although significant shifts could be detected for Re in different oxidation states in various inorganic compounds used as standards. These results give no indication that the perrhenate anion in the organic compounds is significantly affected by its organic molecular environment.
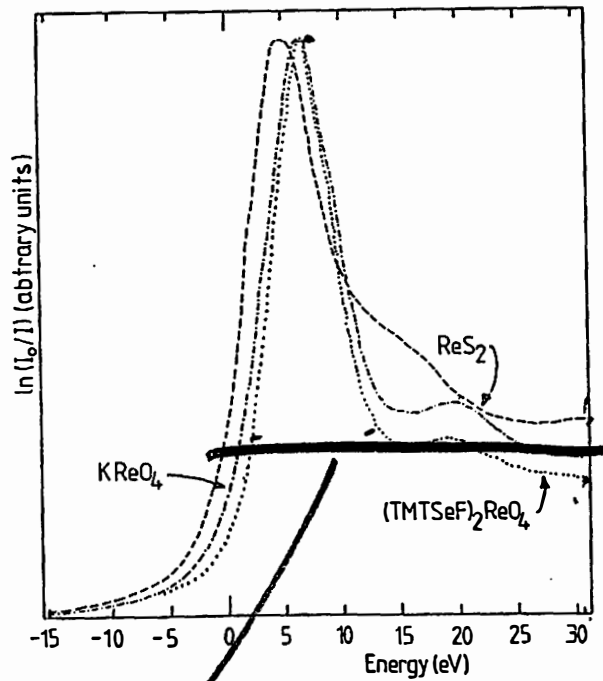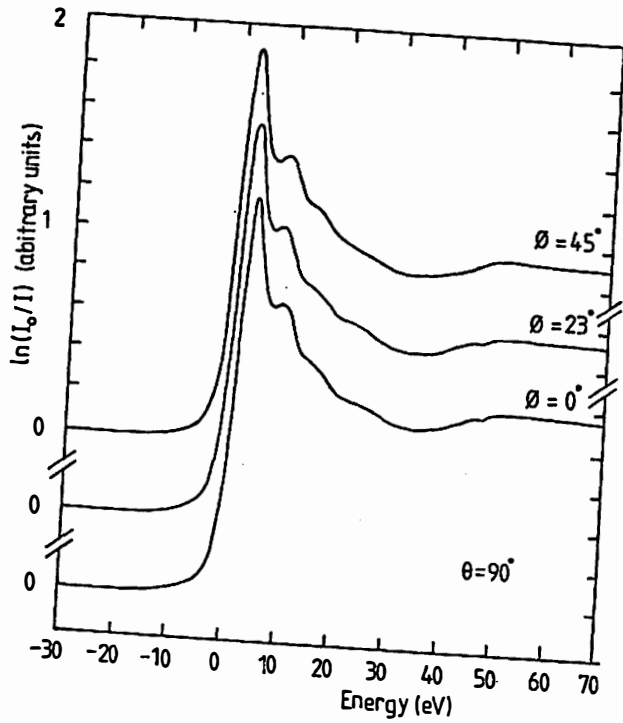
The dependence of the XANES on the polarisation of the incident x-ray beam with respect to the crystal axes of the single crystal samples was examined by varying the sample orientation. The structure on the Re edges was found to be independent of sample orientation. In contrast measurements at the Se K edge in $(TMTSeF)_2ReO_4$ revealed a significant polarisation dependence of the XANES. A shoulder was observed at the edge for E polarised along a, the most conducting axis of the sample. A white peak at the edge is most intense for E perpendicular to a.

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SSRL Synchrotron Radiation

Be Windows

vacuum

Slits

Si Crystal Monochromator

He

I₀

Samples

Gas Proportional Counters

I

Insulation

Ortec PM 265

θ_0

θ_0

Two Si Crystal Ref Planes : (110) & (111)

When normalized to edge jump they do coincide.

$\widehat{aE} = 57^0$

Ø = 57°

Ø = 45°

Ø = 23°

Ø = 0°

$a \parallel E$

θ = 0°

ln(I₀/I) (arbitrary units)

ln(I_0/I) (arbitrary units)

Energy (eV)

-30 -20 -10   0   10   20   30   40   50   60   70

3