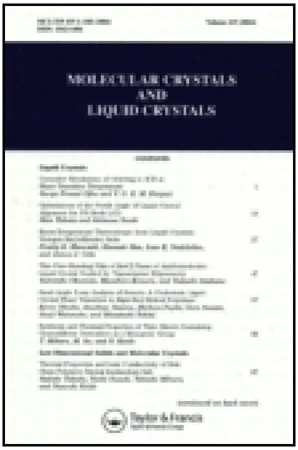

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Asymmetric Broadening of SE($3d_{5/2}$) XPS Spectra of $(TMTSF)_2ClO_4$ and $(TMTSF)_2ReO_4$

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ASYMMETRIC BROADENING OF SE($3d_{5/2}$) XPS SPECTRA OF $(TMTSF)_2ClO_4$ and $(TMTSF)_2ReO_4$

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Abstract A comparison of the x-ray photoelectron spectra in TMTSF, $(TMTSF)_2ClO_4$, and $(TMTSF)_2ReO_4$ shows that the spectra of Se($3d_{5/2}$) for the first is nearly symmetrical, whereas those for the other two are broadened asymmetrically. The broadening is associated with polarization of the selenium by the anion.

INTRODUCTION

X-ray photoelectron spectroscopy is one of the most direct ways of observing the potential and bonding characteristics of electrons at the individual atomic or ionic sites. In the case of $(TMTSF)_2A$ salts, one would expect one-eighth of the selenium atoms in TMTSF to be oxidized, and hence one would expect to observe a small shoulder on the Se($3d_{5/2}$) spectrum. Thus, Ikemoto et al.,[1] attempted to find evidence for such. In addition to well defined valence states, however, more subtle effects attributable to other sources, such as ionicity/covalency and polarization can be observed in the energy distribution curve.[2,3,4] Since it has been suggested that polarization plays a role in compounds like $(TMTSF)_2A$, the presently described study was initiated to investigate what can be found regarding such effects.

EXPERIMENTAL PROCEDURES AND RESULTS

The samples used to obtain the spectra were prepared by pressing single crystals onto stainless steel frits. The crystals were prepared by the usual electrolytic process. Samples were prepared both in air and in a dry box with oxygen and moisture at ppm level. The reported spectra were obtained with MgK_α x-rays in a McPherson ESCA36. The intensities attainable in this instrument with a beryllium window on the x-ray source are such that the Au(4f) spectrum is reproducible within 0.05 eV throughout a scan of 10 eV.

The spectra obtained for TMTSF, $(TMTSF)_2ClO_4$, and $(TMTSF)_2ReO_4$ are shown in Fig. 1. Therein the binding energies and intensities have been shifted so that they coincide respectively in the three cases. As shown, the curve for TMTSF is very nearly symmetrical, but those for the perchlorate and the perrhenate are broadened, largely asymmetrically on the high side of the binding energy and to a greater extent for the perrhenate. The same results were obtained with the samples prepared in air and in the dry box and with MgK_α and AlK_α X-rays. To determine further whether any possible surface oxygen obscured the results, the sample of perrhenate was cleaned in situ with argon-ion bombardment to remove the oxygen in excess of that in the anion. The result was that the curve for the $Se(3d5/_2)$ did not change or changed very slightly.

INTERPRETATION AND SIGNIFICANCE OF BROADENING

There are at least two reasons why the observed broadening cannot be assigned entirely to the increase of the valence of the selenium: (1) On the basis of known shifts of the $Se(3d5/_2)$ energies with valence, a shift of one unit corresponds to approximately leV. Resolution of the observed curve into peaks separated by leV and with an intensity-ratio of 1 to 7 cannot account for the observed asymmetry. (2) The shape of the curve on the low side of the energy indicates some small broadening on this side also. Because a small peak at a displaced energy of leV on the high side does not extend significantly into the low side, the shape on the low side is relatively insensitive to the presence of such a small peak. Thus the source of most of the asymmetric broadening is other than that associated with the increased cationic charge.

Although an adequately quantitative theory of asymmetric broadening of XPS spectra has not been developed, sufficient theoretical studies and empirical observations have been accomplished to identify some of the sources. A small asymmetrical broadening occurs in the case of transition metals (5), and is assigned to a transient potential between the core-hole and the photoelectron. Such broadening presumably cannot occur in insulators. A rather large asymmetric broadening has been reported for U($4f7/_2$) in UO_2(3). Further the broadening is larger for Th($4f7/_2$) in ThO_2 than in ThF_4, and it is larger for U($4f7/_2$) in UO_2 than in UF_4. For a more direct comparison the $3d_{5/2}$ spectra in BaF_2 and BaI_2 was obtained; the broadening is larger in the second compound. de Boer, Haas, and Sawatzky (4) have presented a model in which satellite intensities can be determined from anion polarizabilities. An accompanying feature of these satellites is a decrease in the intensity of the main peak and extensive asymmetric broadening.

Thus, we summarize the situation as follows: (1) The asymmetric broadening of a core-orbital spectrum of a cation can increase with increasing size, and hence polarizability, of an anion. (2) For a given anion, the asymmetric broadening of a cationic core-orbital spectrum increases with increasing polarization of the cation (i.e. Th($4f7/_2$ compared with U($4f7/_2$). From these observations we suggest that the highly polarizable selenium is polarized by the anion and that the polarization is larger for the larger anion, the perrhenate.

Sawatzky[6] has shown that the energy U in the Mott transition criterion, U/W ~1, which measures the electron-electron correlation, can be expressed in terms of the sum of the ionization potential and the electron affinity and a perturbation term expressed as polarization. Thus, if the situation as we describe it has any meaning, then the larger polarization for the perrhenate corresponds to the higher transition temperature and the lower polarization for the perchlorate corresponds to a lower transition temperature, which is directly observable only with the quenched sample.

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REFERENCES

1. T. Ikemoto, K. Kihuchi, K. Yakushi, and H. Kuroda, Solid State Comm. 42 (1982), 257.
2. G. E. Murch and R. J. Thorn, J. Phys. Chem. Solids, 41 (1980), 785.
3. R. J. Thorn, J. Phys. Chem. Solids, 43 (1982), 571.
4. D. K. G. de Boer, C. Haas, and G. A. Sawatzky, Phys. Rev. B29 (1984), 4401.
5. See G. K. Wertheim and S. Hufner, J. Inorg. Nucl. Chem., 38 (1976), 170.
6. G. A. Sawatzky, Solid State Comm. 17 (1975), 569.

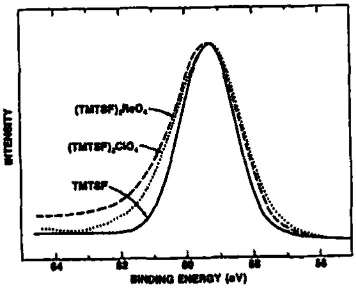

FIGURE 1. X-ray photoelectron spectra of Se($3d5/_2$) in TMTSF, $(TMTSF)_2ClO_4$, and $(TMTSF)_2ReO_4$. Binding energies and intensities have been shifted so that the maxima coincide.