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METAL K-EDGE EXAFS (EXTENDED X-RAY ABSORPTION FINE STRUCTURE) STUDIES OF CrO_2F_2 AND MnO_3F AT 10K

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SUMMARY

I.R. spectroscopy shows that the title compounds are monomeric in the solid state. Metal K-Edge EXAFS data have been obtained from the solids at 10K, and refined to give d(Cr-O) = 1.55Å, d(Cr-F) = 1.71Å, d(Mn-O) = 1.59Å, and d(Mn-F) = 1.72Å.

INTRODUCTION

High oxidation state transition metal fluorides and oxide fluorides are typically very moisture sensitive, highly corrosive, and volatile: properties which mitigate against obtaining reliable structural data. Electron diffraction or microwave spectroscopy are usually used to study the vapour phase structures of such compounds, whilst the definitive method for the solids is X-ray crystallography. However the properties outlined above make production and retention of good quality single crystals experimentally challenging and time consuming, particularly for the more volatile materials. Consequently, very few studies of this type have been reported [1,2]. The availability of synchrotron radiation sources and recent

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improvements in the theory, have made the EXAFS technique a valuable alternative source of structural information [3]. EXAFS is atom-centre specific, does not require single crystals, and moreover, when combined with spectroscopic data to provide symmetry information, can produce an essentially complete local structure determination for highly unstable or reactive materials. We have previously applied this approach to unstable metal complexes [4], to molecules such as Br_2O [5], and to solution species such as $[BrO]^-$ [6]. Here we report for the first time, an extension of this approach to the highly reactive and air sensitive fluorides CrO_2F_2 and MnO_3F, and demonstrate that the approach has wide potential for application to similar reactive species.

EXPERIMENTAL

CrO_2F_2 was made by the static fluorination of CrO_3 at 393K in a Monel autoclave [7]. MnO_3F was made by the method of Aynsley [8] in which anhydrous $KMnO_4$ interacted with IF_5 in pre-fluorinated F.E.P. reactors ($4cm^3$) fitted with P.T.F.E. valves (Production Techniques; STD/VC-6/P) at room temperature. Purification was achieved by condensing the crude product onto a further portion of fresh $KMnO_4$ and allowing the mixture to stand for 1h. at room temperature. In each case the oxide fluoride produced was vacuum-transferred into a pre-fluorinated nickel can fitted with a brass bellows valve (Hoke; 4171M2B) where it could be stored for several days.

CARE: Pure MnO_3F in greater than 0.2g aliquots can detonate violently. Protective shields and clothing must be employed when handling this material.

EXAFS and i.r. spectra of the solids were obtained on samples taken directly from the nickel cans by vacuum tranfer via pre-fluorinated copper spray-on tubes. I.R. spectra of the solids and of the compounds isolated in nitrogen matrices, both at 10K, were obtained using the equipment described elsewhere [9]. The purity of the oxide fluorides was also checked before and after the EXAFS experiments using i.r. spectroscopy.

The EXAFS data were collected at the Daresbury Synchrotron Radiation Source operating at 2GeV with an average current of

190mA using the cryostat described previously [10]. The oxide fluorides were condensed from the vapour phase onto a 0.25mm thick Be window cooled to 10K, the thickness of the deposit being monitored by measuring the height of the appropriate absorption edge. Data were collected in transmission mode on station 8.1 (Cr), and on station 7.1 (Mn) using order-sorting Si(111) monochromators. Data for K_2CrO_4 and $KMnO_4$, which served as model compounds, were collected at room temperature from the powdered solids diluted with boron nitride. Data treatment utilized the programs PAXAS [11] and EXCURVE [12]. Several data sets were collected on each compound, checked for the absence of anomalies, and subsequently averaged. The pre-edge background was removed by fitting the spectrum to a cubic polynomial, and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using polynomials, and the optimum function judged by minimising the intensity of chemically insignificant shells at low r in the Fourier transform. Curve fitting used single scattering curved-wave theory with phase shifts and back-scattering factors calculated using the normal ab initio methods [12].

RESULTS AND DISCUSSION

The major features in the i.r. spectra of CrO_2F_2 and MnO_3F are listed in the Table. Although the absorptions in the spectra of the solids are slightly shifted from those in the vapour phase, the overall close similarities in vibration frequencies clearly show that these two compounds in the solid state exist as molecular monomers. Structural data for the vapour phase monomers have been obtained by electron diffraction for CrO_2F_2 [13] and microwave spectroscopy for MnO_3F [14]. Here we report data for the solids at 10K obtained from the metal K-edge EXAFS data. The reliability of the data collection and treatment was confirmed by collection and analysis of metal K-edge EXAFS data on two model compounds, $KMnO_4$ and K_2CrO_4. The results are in very satisfactory agreement with the single crystal X-ray data. In particular, for $KMnO_4$ our EXAFS studies yielded d(Mn-O) = 1.61Å compared with the X-ray value of 1.607(5)Å [15], whilst for K_2CrO_4 corresponding bond lengths are 1.64Å, and 1.643Å (mean) [16] respectively.

TABLE

Spectroscopic and structural data[a]

	CrO_2F_2		MnO_3F	
	gas	solid	gas	solid
ν(M-O)/cm^{-1}	1016,1006[b]	1005[c]	952,905[d]	950,905[c]
ν(M-F)/cm^{-1}	789,727	770,710	721	705
d(M-O)/Å	1.575(2)	1.55[e] 1.55[f]	1.586(5)	1.58[e] 1.59[f]
$2\sigma^2$/Å^2 [g]		0.003 0.002		0.006 0.006
d(M-F)/Å	1.720(2)	1.71[e] 1.71[f]	1.724(5)	1.73[e] 1.72[f]
$2\sigma^2$/Å^2		0.010 0.010		0.020 0.020
FI[h]		1.09 0.80		2.38 1.91
R[i]		22.9 19.4		18.6 16.8

[a] with current data analysis packages, the errors in the EXAFS determined bond lengths are ±0.02Å. [b] Reference 18. [c] ± 5cm^{-1}. [d] Reference 19. [e] 2-shell fit. [f] 3-shell fit. [g] Debye-Waller factor. [h] Fit index $\Sigma_i[(\chi^T-\chi^E)k^3_i]^2$.

[i] R factor $[\int(\chi^T-\chi^E)k^3dk/\int\chi^E k^3dk] \times 100\%$.

The fit of the EXAFS data for CrO_2F_2 was initially based on a two shell model with the occupation numbers fixed on the basis of the stoichiometry and the i.r. data, and the resulting EXAFS parameters are listed in the Table. In addition to prominent features due to the directly bonded O and F the Fourier transforms also showed a reproducible feature at ca 3Å, which we attribute to backscattering by adjacent molecules, and our final refinement included a third shell to take account of this. Figure 1 shows the background subtracted EXAFS and the Fourier transform for the three shell model. The Cr-O and Cr-F bond lengths obtained from the solid are very similar to those of the gas phase monomer [13], as would be expected from the essentially molecular nature of the solid, and the position of the third shell is consistent with packing based upon Van der Waals radii.

In the case of MnO_3F similar refinement based upon two shells yielded only a single broad feature in the Fourier transform (Figure 2). In order to demonstrate the two shell model is valid in this case, we also fitted the data to a single shell of four oxygens. Comparison of the refined data from the two models showed a 10% decrease in R-factor and a statistically significant [17] decrease in the fit index for the two-shell model. Moreover the correlations in the two shell fit were within acceptable limits, and hence we conclude that in this case also, the data satisfactorily define to distinguish the Mn-O and Mn-F distances (Table). For this species our EXAFS studies also revealed a third shell at ca 3Å, similarly attributable to neighbouring molecules.

For both CrO_2F_2 and MnO_3F, comparison between the two and three shell models showed (Table) negligible differences in bonded distances, and although the addition of the third shell is statistically justified [17] in both cases, the occupation numbers are not well-defined: presumably as a result of imperfect packing.

CONCLUSION

This work has shown that the title compounds are molecular in the solid state and has provided bond length data for the

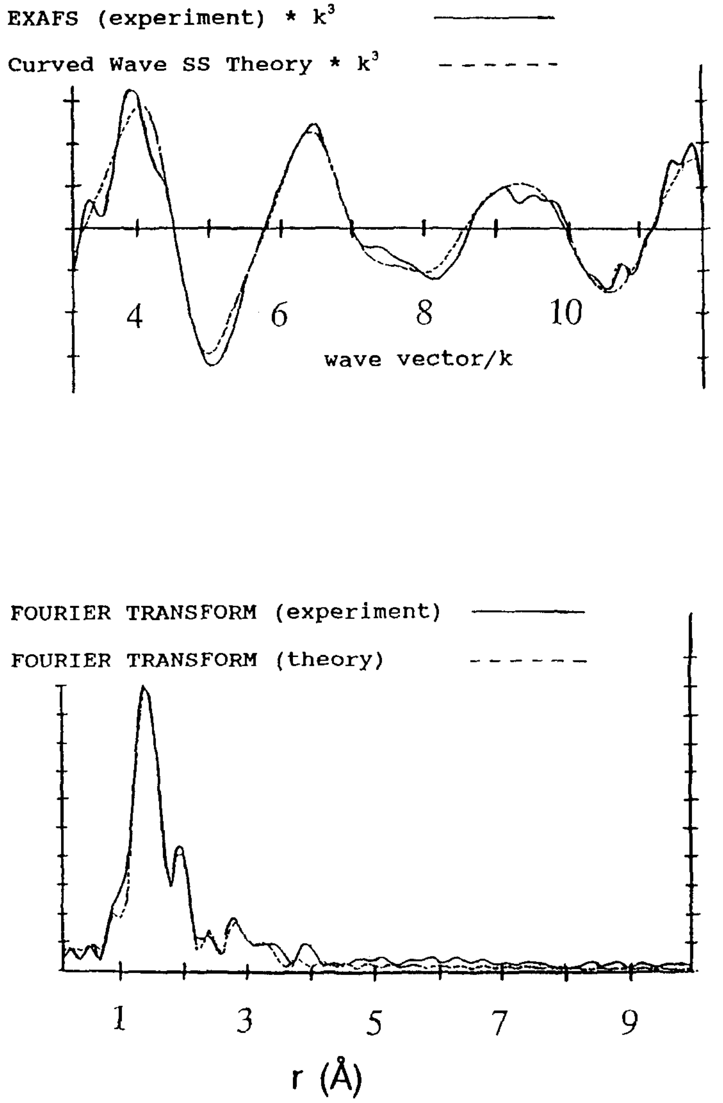

Fig.1. EXAFS and Fourier transforms for solid CrO_2F_2

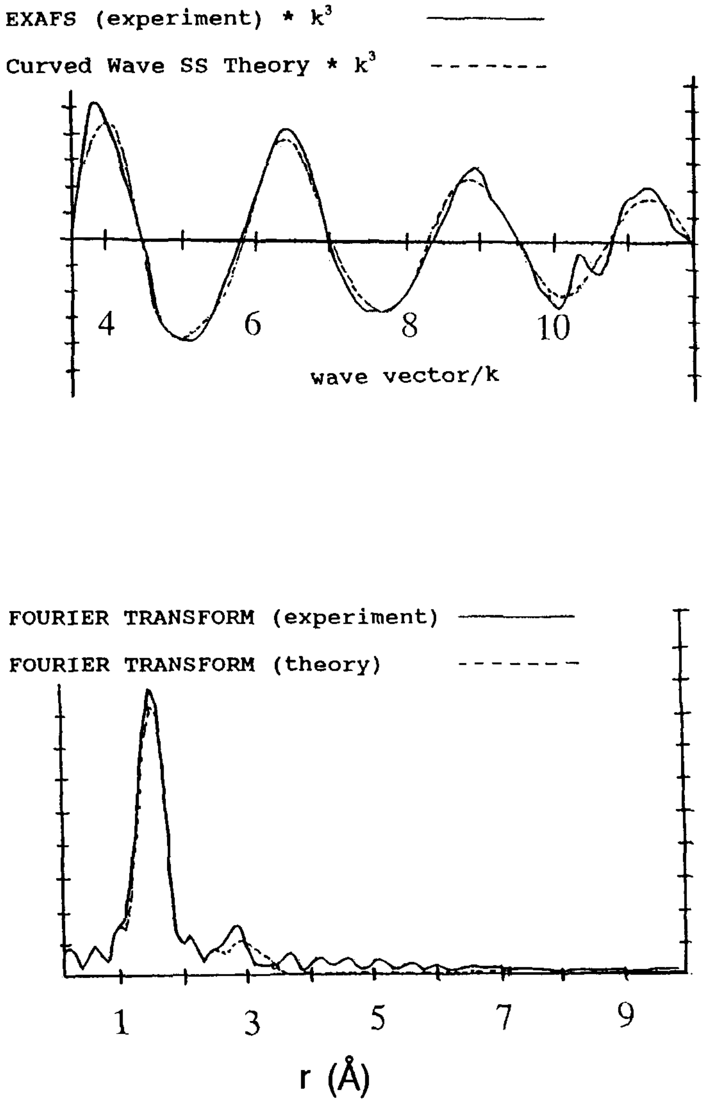

Fig.2. EXAFS and Fourier transforms for solid MnO_3F.

solids. Of more general significance is the fact that EXAFS data in combination with a suitable spectroscopic probe can provide structural data for highly reactive or unstable oxide fluorides. In particular this approach is capable of distinguishing M=O from M-F in such compounds, and will therefore be of value in many related systems.

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