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EXAFS of a tetragonally compressed Cu(II) compound

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EXAFS has been used to show that at room temperature in KCuAlF₆, the copper(II) centre is in a distorted tetragonally compressed octahedral environment. The bond lengths determined (1.88 (×2), 2.12 (×4) Å) are in good agreement with the X-ray crystal structure.

Keywords: EXAFS; copper; compressed.

1. Introduction

The preferred geometry for copper(II) with six identical ligands is a tetragonally elongated octahedron. This geometric distortion is a consequence of the Jahn-Teller Effect.

KCuAlF₆ is an interesting complex in that it is one of the few copper(II) compounds where the six co-ordinate copper experiences a tetragonal compression. The crystal structure determination of KCuAlF₆ indicated that the copper(II) exists in a tetragonally compressed octahedron. (Wingefeld & Hoppe, 1984) A tetragonally compressed geometry is rare, but not unknown. (Dubicki *et al.*, 1989; Friebel *et al.*, 1976; Riley *et al.*, 1988) The other examples of compressed geometries involve either doped crystals where the compression is "forced" on the copper by the host lattice, or compounds which have two different ligands, where the compression is associated with one ligand having a stronger ligand field than the other. KCuAlF₆ is *unique* in that it is the only example of a pure Cu(II) compound with just one ligand type which has a compressed tetragonal geometry.

There have been other examples where the crystallographic structure indicates a compressed geometry. However, it can usually be shown that the copper(II) centre is actually in a tetragonally elongated environment, and it is disorder within the structure which gives the appearance of a tetragonal compression to an X-ray crystal structure determination. (Ellis *et al.*, 1994; Villain *et al.*, 1997)

In 1990, Finnie *et al.* measured the unpolarised low temperature absorption spectrum of a single crystal of KCuAlF₆. (Finnie *et al.*, 1990) Ligand field calculations indicated that for a tetragonally elongated copper(II) centre, there would be one main magnetic dipole origin, corresponding to the transition between B_{1g}(x²-y²) → B_{2g}(xy) orbital states. For a tetragonally compressed centre, there would be two magnetic dipole origins calculated to have comparable intensities. These origins correspond to the transitions to the spin-orbit split components of the A_{1g}(z²) → E_g(xy,yz) orbital states. The low temperature absorption spectrum showed two sharp origins, indicating that at low temperature the copper centre in KCuAlF₆ is in a tetragonally

compressed environment. The magnitude of the spin-orbit splitting implied a relatively large compression. (Finnie *et al.*, 1990)

In a previous study of the unusual magnetic properties of the compound, it was suggested that an orthorhombic distortion might be present, with this being masked in the X-ray analysis by disorder. (Atanasov *et al.*, 1993) In order to test this possibility, and establish the local co-ordination geometry independent of the crystal structure data, we have studied the EXAFS of the compound.

2. Results and Discussion

The unprocessed EXAFS data is shown in Figure 1. A sharp monochromator glitch was removed from 9.673 keV. The filtered experimental and calculated EXAFS, as well as the *k* window used are shown in Figure 2. The experimental and calculated Fourier-transform amplitude of the EXAFS, as well as the R window used are shown in Figure 3.

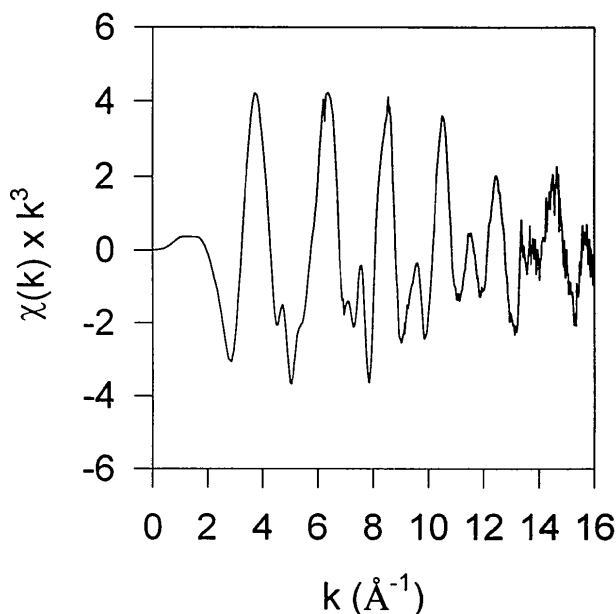


Figure 1
Unprocessed EXAFS of KCuAlF₆.

Using only the first co-ordination shell and single scattering theory, FEFF4 (Rehr *et al.* 1991), several models were investigated. Models tested included those with varying degrees of tetragonal elongation and compression, D_{2h} and O_h. After preliminary results indicated that the copper centre was in a tetragonally compressed environment, the model was extended to include atoms within 5 Å, and multiple scattering was used.

The observed EXAFS was well matched by the EXAFS calculated after refinement of the model with two short and four long bonds. The short bonds (1.88 (×2) Å) and long bonds (2.12 (×4) Å) are in good agreement with the crystallographic values (1.783, 1.881, 2.122 (×2), 2.124 (×2) Å). (Wingefeld & Hoppe, 1984) The goodness-of-fit parameter, R, was calculated from $R = \sqrt{\chi^2 / \chi^2_{\text{calc}=0}}$, where χ^2 is the quantity minimised in the refinement and $\chi^2_{\text{calc}=0}$ is the value of χ^2 when the calculated EXAFS is uniformly 0. The final R-value was 0.185.

The local geometry of copper(II) in KCuAlF₆ is a distorted tetragonally compressed octahedron. (Wingefeld & Hoppe, 1984) The FCuF angles involving the equatorial fluorides are unequal with three of the angles approximately 80° and the fourth angle

approximately 118° . The FCuF angle with the axial fluorides is approximately 171° . The equatorial fluorides bridge to neighbouring aluminium ions and the axial fluorides bridge to neighbouring copper ions. KCuAlF_6 is therefore a polymeric structure with chains of aluminium octahedra and copper octahedra linked with bridging fluorides.

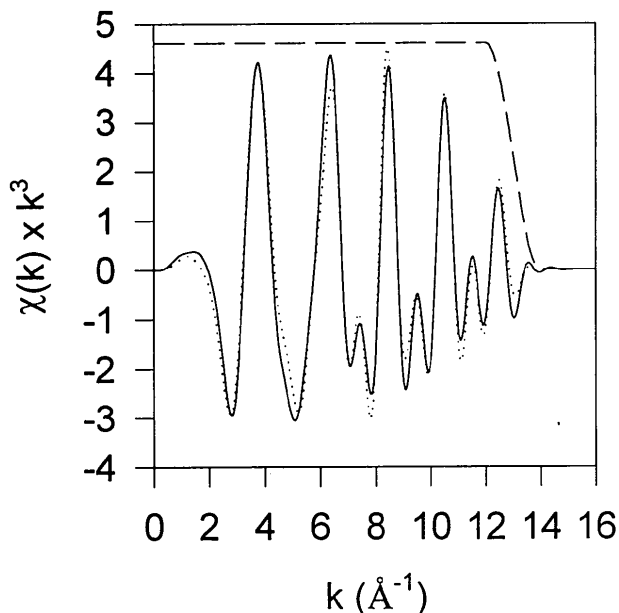


Figure 2
The filtered EXAFS of KCuAlF_6 : observed (—), calculated from refined model (.....), window used in Fourier Filter (---)

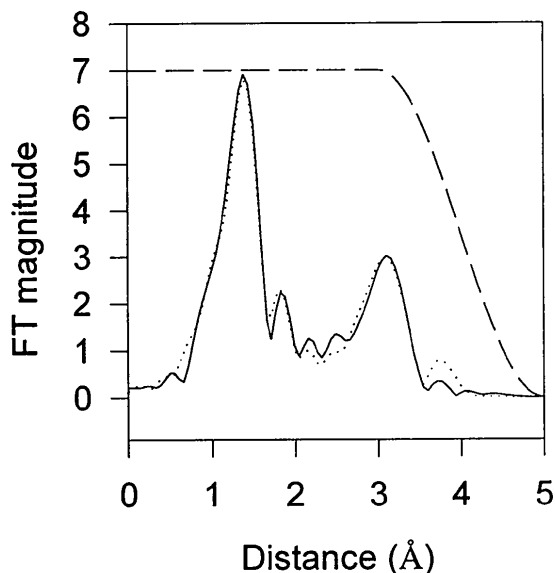


Figure 3
Fourier-transform amplitude of EXAFS: observed (—), calculated from refined model (.....), window used in Fourier Filter (---)

The Debye-Waller temperature factors were observed to be higher for the equatorial fluorides ($0.029(1) \text{ \AA}^2$) than for the axial fluorides ($0.005(1) \text{ \AA}^2$). This trend was also observed for the thermal ellipsoids in the crystal structure. (Wingefeld & Hoppe, 1984) This may be due to the difference in bonding for the two types of fluorides. The axial fluorides bridge between two copper ions and the equatorial fluorides bridge between a copper ion and an aluminium ion. Another explanation could be a low frequency

vibration connected with the Jahn-Teller distortion.

Future work will include the temperature dependent structure of the compound using EXAFS. Previous studies on doped tetragonally compressed copper(II) complexes have been shown to have temperature dependent electronic structure. (Riley *et al.*, 1986) This is due to competing effects of the tetragonal compression imposed by the host on the natural tendency of Cu(II) complexes to adopt an elongated geometry, resulting in a soft vibrational mode.

This low energy vibration is the orthorhombic component of the Jahn-Teller active e mode and is thought to be partially responsible for the higher Debye-Waller factors for the equatorial fluorides.

It has been observed that in CsAgAlF_6 (Müller, 1981) and KZnAlF_6 (Wingefeld, 1984) the Ag^{2+} and Zn^{2+} ions also occur in tetragonally compressed environments. However, in both of these examples the distortion is significantly less than the copper(II) analogue. From this, it can be deduced that while the lattice plays a significant role in determining the observed sign of the tetragonal distortion, the Jahn-Teller Effect contributes to the magnitude of the distortion.

3. Conclusions

EXAFS has been used to probe the local geometry of copper(II) in KCuAlF_6 . The results are consistent with the crystal structure determined at room temperature, confirming that in KCuAlF_6 , the copper(II) ion exists in a compressed octahedral geometry at room temperature.

In all other crystal structures of pure Cu(II) compounds with a reported tetragonal compression of six equivalent ligands, it has been subsequently shown that this is a result of a disordered arrangement of elongated geometries. KCuAlF_6 is unique in that both the crystal structure and EXAFS unambiguously confirm the copper(II) is tetragonally compressed.

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References

- Atanasov, M., Hitchman, M.A., Hoppe, R., Murray, K.S., Moubaraki, B., Reinen, D. & Stratemeier, H. (1993) *Inorg. Chem.* **32**, 3397-3401.
- Dubicki, L., Krausz, E.R., Riley, M.J. & Yamada, I. (1989) *Chem. Phys. Lett.* **157**, 315-320.
- Ellis, P.J., Freeman, H.C., Hitchman, M.A., Reinen, D. & Wagner, B. (1994) *Inorg. Chem.* **33**, 1249-1250.
- Finnie, K., Dubicki, L., Krausz, E.R. & Riley, M.J. (1990) *Inorg. Chem.* **29**, 3908-3910.
- Friebel, C., Propach, B. & Reinen, D. (1976) *Z. Naturforsch.* **31b**, 1574-1584.
- Müller, B.G. (1981) *J. Fluorine Chem.* **17**, 317-329.
- Rehr, J.J., Mustre de Leon, J., Zabinsky, S.I. & Albers, R.C. (1991) *J. Am. Chem. Soc.* **113**, 5135-5140.
- Riley, M.J., Hitchman, M.A. & Reinen, D. (1986) *Chem. Phys.* **102**, 11-28.
- Riley, M.J., Hitchman, M.A., Reinen, D. & Steffen, G. (1988) *Inorg. Chem.* **27**, 1924-1934.
- Villain, F., Verdagner, M. & Dromzee, Y. (1997) *J. Phys. IV.* **7(C2-Part1)**, 659-670.
- Wingefeld, G. (1984) PhD Thesis, Institute for Inorganic and Analytical Chemistry, Giessen, Germany.
- Wingefeld, G. & Hoppe, R. (1984) *Z. anorg. allg. Chem.* **516**, 223-228.

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