ELECTRONIC STRUCTURE AND ELECTRIC FIELD GRADIENT TENSOR IN POTASSIUM FERRICYANIDE

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Résumé.— Des techniques de calcul LCAO-MO et de tenseur d’intensité ont été utilisées pour étudier la structure électronique et le gradient de champ électrique dans le ferrocyanure de potassium. On trouve qu’il est nécessaire d’inclure les effets dus à l’existence de deux sites de fer non équivalents et des effets de polytypisme pour rendre compte des effets expérimentaux.

Abstract.— LCAO-MO and intensity tensor techniques have been employed to study the electronic structure and electric field gradient tensor in potassium ferricyanide. It is found necessary to include the effects of non-equivalence of the two iron sites and polytypism for the agreement with the experimental results.

1. Introduction.— The structural, electronic and magnetic behaviour of potassium ferricyanide, $K_{3}Fe(CN)_{6}$, has been the subject of rather intensive experimental and theoretical investigations, due to the fact that the ferricyanide complex is considered as a typical example for covalent bonding and strong interaction between the ferric ion and the ligand field. From X-ray structural investigations /1,2/, the unit cell of $K_{3}Fe(CN)_{6}$ has been described as monoclinic, orthorhombic or pseudoorthorhombic. This controversy concerning the crystal structure arises from the occurrence of polytypism due to the different stacking periodicities of the basic monoclinic cell. However, each unit cell contains two crystallographically different iron sites, $Fe_1$ and $Fe_2$, both surrounded by a distorted octahedron of six CN~ groups. The electronic structure for the ferricyanide complex has been also studied extensively using the ligand field theory formalism /3,5/, taking into account its low symmetry components, and spin-orbit coupling. However, these components are considered not to be affected by polytypism. The nuclear quadrupole interaction, magnetic susceptibility and their temperature dependence has been calculated with various models. These calculations with a temperature invariant ligand field do not explain the experimental results obtained from Mössbauer and magnetic susceptibility measurements with powder samples in the temperature range 4.2 – 300 K.

Single crystal Mössbauer measurements in the paramagnetic region have also been carried out. The dependence of the ratio area of the two quadrupole partners on the direction of the $\gamma$-rays relative to the crystal structure has been studied accurately /4/ but without taking into account the non-equivalence of the two iron sites and polytypism. These results are inconsistent with the expectation from the crystal structure that the principal axes of the EFG tensor at the two Fe$^{3+}$ sites lie in the directions of elongation of the cyanide octahedra.

In view of the uncertainties about the structural, electronic and magnetic properties of $K_{3}Fe(CN)_{6}$, we have looked again at the ferricyanide complex in two ways; (i) the experimental single crystal Mössbauer results are analysed using Zimmermann's intensity tensor method /6/, and (ii) molecular orbital calculations are performed based on $K_{3}Fe(CN)_{6}^{5+}$ clusters using Fe (3d, 4s, 4p) C and N (2s, 2p) and K (4s) atomic orbitals. In both cases, the non-equivalence of the two iron sites and the polytypism in potassium ferricyanide are considered.

2. Re-analysis of single crystal Mössbauer data.— Recently, Zimmermann /6/ has proposed a method to evaluate an EFG tensor from the intensity analysis. It is based on the fact that main components of EFG tensor can be directly represented by an intensity tensor, $I$. Its principal components have following three properties:

(i) The asymmetry parameter of the EFG is given by

\[ \eta = (I_{xx} - I_{yy}) / I_{zz} \]

(ii) The maximum absolute value of $I_{pp}$, i.e. $I_{zz}$, has the same sign as $V_{zz}$.

(iii) The test factor $I_{AA}$, defined in the same way...
as the square of the quadrupole splitting, is constant
and unity, i.e. \( I_0 = 16 \, \text{T}^2 \) (1+3n^2) = 1.
These properties show that the traceless intensity
tensor and the EFG tensor are proportional. Our re-
analysis of the available data on intensity ratios
from the single crystal measurements (modified to
zero-absorber thickness) clearly show three inter-
esting results; (i) it is possible to take into ac-
count the effects of two non-equivalent iron sites
and polytypism (ii) the orientation of \( y_{Zz} \), as
derived by Oosterhuis and Lang /4/, is one possible
solution out of a manifold of other solutions, and
(iii) the orientation of \( V_{zz} \) components of the lo-
cal EFG tensors is perpendicular to the quasitetra-
gonal axis. It must be pointed out that it is in
contrast to what usually is found in ionic compounds,
namely that the direction of the V component is
parallel to the axis along which the largest distor-
tion is observed.

3. Semi-empirical LCAO-MO calculations.- We have
performed semi-empirical molecular orbital calcula-
tions /7/ for each of the two iron sites in the fer-
rycianide complex, based on KFe(CN)\(_4\) clusters,
using Fe (3d, 4s, 4p) C and N (2s, 2p) and K (4s)
atomical orbitals. The ferricyanide complex is rep-
resented by different cluster geometries, known at
95 and 300 K, for the two iron sites. From the linear
combination of the basis set of 65 atomic orbitals,
MOs are constructed, which are occupied by 65 elec-
trons with a total spin \( \frac{1}{2} \). The valence shell
populations for the two iron sites are \( \phi_{1}, \phi_{2}, \phi_{3} \)
\( 3d^{6-4s} \) and \( \phi_{3} \) \( 3d^{6-4s} \) and \( \phi_{1} \) \( 3d^{6-4s} \) and \( \phi_{2} \) \( 3d^{6-4s} \). The ligand field splitting parameter (10Dq)
is about 32000 cm\(^{-1}\) for Fe, site and 31500 cm\(^{-1}\) for
Fe, site, which is comparable with the experimental
value of 35000 cm\(^{-1}\). The three populated MOs which
are highest in energy \( \phi_{1}, \phi_{2}, \phi_{3} \) see in Fig.1a)
are of mainly iron character with a covalency factor of
about 0.8.

It may be recalled that from the analysis of
earlier ESR experiments a covalency factor of 0.875
has been found as one of the solutions in fitting
the data. A limited configuration interaction (CI)
calculation is then performed on three configurations
\( \psi_{1}, \psi_{2}, \psi_{3} \) (as defined in Fig. 1a) resulting in
three CI states \( \psi_{CI}^{1}, \psi_{CI}^{2}, \psi_{CI}^{3} \), which remained
nearly pure, but their energy sequence is interchan-
ged : \( \psi_{CI}^{1} = \psi_{i} \), \( \psi_{CI}^{2} = \psi_{j} \), and \( \psi_{CI}^{3} = \psi_{k} \). We then take
into account spin-orbit coupling among these three
CI states by a first-order perturbation treatment,
resulting in an energy level diagram shown in figure
1(b). In order to calculate the temperature depen-
dence of quadrupole interaction, we temperature ave-
rage the EFG tensors for the two iron sites ac-
cording to Boltzmann statistics. This is applicable in
the case of KFe(CN)\(_4\), since we are in the fast
relaxation limit due to strong spin-lattice interac-
tion. From a detailed analysis, we find for the two
iron sites that their energies \( \Delta_{1} \), \( \Delta_{2} \) and their
calculated Mössbauer parameters, \( V_{zz}, \eta \) and \( \Delta_{E} \) are
differently. The orientation of \( V_{zz} \) (Fe\(_1\)) and
\( V_{zz} \) (Fe\(_2\)) with respect to the a'bc axes system devia-
to some extent compared to the orientation obtai-
ned from the intensity tensor analysis.

Figure 2(a) shows the temperature dependence of \( \Delta_{E} \) calculated on the basis of the structural
data obtained at 95 K and 300 K. From the curves,
it is obvious that the experimental \( \Delta_{E} \) values
in the temperature range \( T < 130 \) K can only be fitted
with temperature dependent structural data i.e. with
temperature dependent ligand field parameters \( \Delta_{1} 
and \( \Delta_{2} \). Figure 2(b) shows the temperature dependence of \( \Delta_{1} \) and \( \Delta_{2} \) necessary for fitting the experimental
\( \Delta_{E} \) variation. These results are in qualitative
agreement with the temperature dependent ligand field
model used in a earlier study /8/.

4. Conclusions.- Our analysis of available experi-
mental Mössbauer data using intensity tensor and

\[
\begin{align*}
\psi_1 & = 0.003 \langle 13dx^2 \rangle - 0.012 \langle 13dy^2 \rangle - 0.890 \langle 13dz^2 \rangle - 0.081 \langle 13dyz \rangle - 0.011 \langle 13dx \rangle \\
\psi_2 & = 0.010 \langle 13dx^2 \rangle + 0.666 \langle 13dyz \rangle + 0.056 \langle 13dx \rangle + 0.068 \langle 13dy \rangle - 0.006 \langle 13dyz \rangle \\
\psi_3 & = 0.037 \langle 13dz^2 \rangle + 0.064 \langle 13dy \rangle + 0.052 \langle 13dx^2 \rangle - 0.066 \langle 13dyz \rangle - 0.004 \langle 13dx \rangle \\
\end{align*}
\]

doubly occupied MO's \( \phi_i \) 1s \leq 30.

Fig. 1a : LCAO MOs \( \phi_i \) (i = 31, 32, 33) in KFe(CN)\(_4\) calculated with the cluster geometry obtained
at 95 K. The coordinate system used in the MO calculations is the following :
x is parallel to the axis which connects the two CN\(^-\) groups having maximum Fe-C distance and y is
parallel c-axis.
LCAO-MO method have established the electronic structure of the ferricyanide complex, which is in reasonably good agreement with the published work.

Fig. 1b: Many electron CI states $\psi^{CI}_i (i=1, 2, 3)$ together with their energy separations $\Delta_1$ and $\Delta_2$ in $K_3Fe(CN)_6$.

Further details of our study, including the computation of electron density at the iron nucleus, magnetic susceptibility and gyromagnetic tensors and their comparison with experimental results will be published elsewhere.

Fig. 2: a) Temperature dependence of quadrupole splitting, $\Delta E_2(T)$, of $K_3Fe(CN)_6$ which is a 1:1 average from $Fe_1$ and $Fe_2$ sites. Curve a is calculated with the 300 K cluster geometry; curve b corresponds to the 95 K cluster geometry, however, assuming temperature dependent energy separations $\Delta_1$ and $\Delta_2$ as shown in figure 2b.

b) Temperature dependence of energy separations $\Delta_1$ and $\Delta_2$ of $K_3Fe(CN)_6$ for $Fe_1$ and $Fe_2$ site. Curves 2 and 3 correspond to $\Delta_1$ and $\Delta_2$ of $Fe_1$; curves 1 and 3 correspond to $Fe_2$.

References

9/ Reschke, R., Trautwein, A., Harris, F.E. and Date, S.K., to be published in Phys. Rev. B.