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CRYSTAL FIELD SPLITTING IN UO$_2$: AN INTERMEDIATE VALENCE COMPOUND?

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1. INTRODUCTION

In the study of the electronic structure of actinide materials the major problems are the questions of the spatial extent of the 5f-electrons, the magnitude of the crystalline electric field (CEF) in these materials, the degree of overlap and possible hybridization of the electron wave functions which can produce intermediate valence states.

The actinide 5f-electrons are generally less localized than the 4f-electrons of the rare earth (RE) but less itinerant than the transition metal 3d-electrons. Because of this one might expect magnetic properties ranging from that of itinerant 3d-systems to this of localized 4f-systems. Indeed, the heavy actinides starting with plutonium, are very similar in their physical properties to the light rare earth metals (REM) [1]. Information about the spatial distribution of the 5f-electrons may be obtained from magnetic form factor measurements by neutron diffraction. The localization of the 5f-electrons can be proved by measurements of the CEF-levels using spectroscopic methods. In the REM the inelastic neutron scattering (INS) has been proved to be a very powerful method for measuring the transitions between the CEF-levels. Because of the more pronounced spatial extention of the 5f-electron wave functions, the CEF-splitting in the actinides is expected to be about an order of magnitude larger (200-300 meV) than in the corresponding RE compounds (20-30 meV) [2]. The great overall splitting of the 5f-electron multiplets makes the study of the CEF by INS difficult due to the relatively low intensity of high energy neutrons in the spectrum of thermal neutrons from the reactor. For this reason, there are no measurements of the whole spectrum of CEF-transitions in any actinide compound up to now. Only a few measurements of low-energy CEF-transitions in actinides are known [2] which do not give an interpretation of the CEF in these compounds. The interpretation of the experimental spectra in the actinides is further complicated by the fact that the real valence of the most of actinide compounds is not definitely known. Because of the relatively extended 5f-electron wave functions, one expects to find more examples of valence instabilities and intermediate valence states among actinide materials than among the RE.

In this paper we present the first direct observation of CEF-transitions in the paramagnetic state of the actinide compound UO_2 in an energy region up to 200 meV. A theoretical interpretation of the experimental data is not possible within the conventional CEF-theory J-mixing effects included [3]. Assuming that the real valence and thus the 5f-electron configuration in UO_2 has not in each case an integer value, we were able to interprete the experimental spectra on the basis of an intermediate valence state and valence fluctuations.

2. EXPERIMENT

Uraniumdioxid is an ionically bounded semiconductor which has a simple type - I antiferromagnetic order below 30.8 K.

In this paper we describe measurements of inelastic magnetic neutron scattering at the uranium ion in the paramagnetic state of UO_2 at a temperature of 80 K. A powdered sample of UO_2 was used in our experiments. By neutron diffraction study no contribution from other phases or internal distortions at 80 K could be observed. In order to get information about the phonon contribution in the INS experiment, we also measured the isostructural compound ThO_2 representing also a single-phase sample.

The INS experiments were performed with a time-of-flight spectrometer in the inverted geometry with a beryllium filter in front of the detector at the IBR-30 pulsed reactor at JINR Dubna. The spectrum obtained from the UO_2 sample at a temperature of 80 K and a scattering angle of $\phi = 60°$ is shown in figure 1. ThO_2 also was studied under the same experimental conditions. In the spectrum of UO_2 a very broad peak was observed with the intensity maximum in the channel number range from 300 to 340. To be able to separate the magnetic part of the scattering it is necessary to know the phonon spectrum. Young [4] calculated the phonon density of state $Z(\omega)$ for UO_2 using experimental phonon dispersion curves [5]. They found that the oxygen part of the phonon frequency distribution is sufficiently separated from the uranium part. Therefore, the differential phonon cross section for oxygen and uranium could be calculated separately. The resulting spectrum is shown by the dotted line in figure 2. To subtract this phonon part from the INS spectrum it is necessary to know how to normalize the calculated spectrum to the measured one. Therefore, we studied the spectrum of inelastically scattered neutrons at a sample of the isostructural compound ThO_2 under
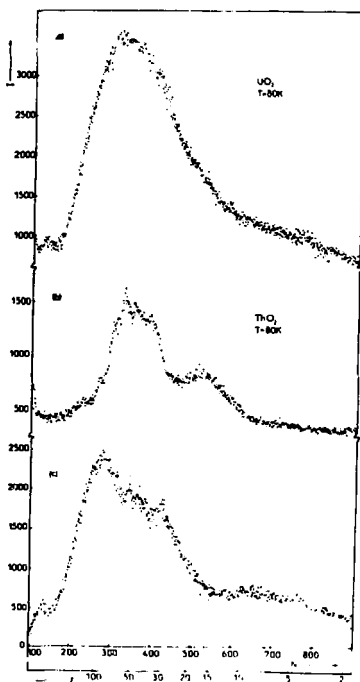
Fig.1. Experimental neutron spectra (a) UO_2, T = 80 K, $\phi = 60°$; (b) ThO_2, T = 80 K, $\phi = 60°$ and (c) magnetic part of the neutron spectrum in UO_2.

the same conditions as for UO_2. The spectrum of ThO_2 is shown in figure 2 by the full line. We find a good agreement between the calculated phonon contribution and the neutron spectrum, based on the phonon density of states from UO_2, and the experimental neutron spectra of ThO_2. Therefore we assume that the measured spectra of ThO_2 is equivalent to the phonon contribution in the spectrum of UO_2 as it can be seen in figure 1. The measured ThO_2 spectrum (with background corrections) was normalized to the UO_2 spectrum taking into account the corrections due to different measuring time, sample volume and incident neutron flux. The difference spectrum shown in figure 1 is considered to be a pure magnetic part of the INS spectrum for UO_2.

We found three CEF transitions which can be characterized by the following parameters:

energy (meV)	relative intensity	FWHM (Gaussian shape, meV)
130	1	70
80	1/3	60
32	0.12	33

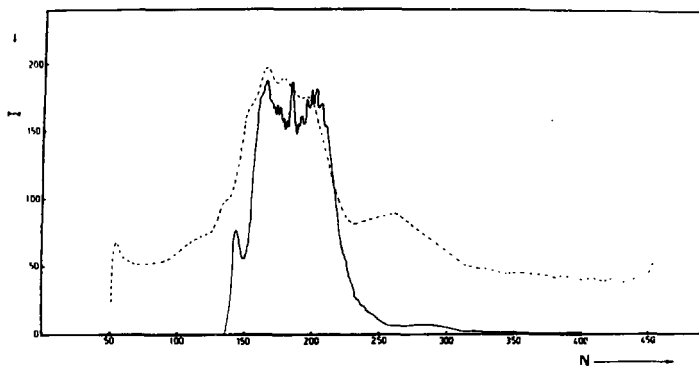The values in the table are correlated to each other and the errors are of about 10%.

Fig.2. Calculated phonon contribution to the neut-
ron spectrum, based on the phonon density of
states for UO_2- full line; and experimental neutron
spectrum of ThO_2 ($T = 80$ K, $\phi = 60°$) – dotted line.

3. INDICATION FOR INTERMEDIATE VALENCE STATES IN UO_2

Because of its complex magnetic and electronic behaviour,
UO_2 is one of the most intensively studied actinide compounds.
The mechanism responsible for the first order transition to
the antiferromagnetic state was often discussed in the past.
Blume[6] argued that in the paramagnetic phase the ground
state is the Γ_1-singlet and at ordering temperature T_N
a crossing occurs with the Γ_5-triplet. The properties of the
ground state wave function in UO_2 have been considered by
Rahman and Runciman[7]. Fitting the observed magnetic moment
with realistic crystal field – and spin orbit parameters, they
showed the Γ_5-triplet to be always the ground state. Measure-
ments of the magnon dispersion curves in the antiferromagne-
tic phase[8] of the magnetic susceptibility[9] and infrared
spectroscopy[10] are all consistent with the triplet Γ_5 being
the ground state. The first excited level in the work by
Rahman and Runciman[7] was predicted to be the Γ_3-doublet
at an energy of 170 meV. Neither this nor any other higher
excited level have been experimentally observed. All these in-
terpretations assume for the uranium ions in UO_2 an ionocity
of U^{4+},i.e., a configuration of two 5f-electrons per ion and
ignore the possibility of having a mixed valence state in UO_2.

On the other hand, recent band calculations[11] for actinide
compounds predict small valence excitation energies. These

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valence excitation energies in the actinide dioxides decrease
with increasing atomic number [12].

Self-consistent molecular-orbital cluster calculations
give a configuration value of 2.71 5f-electrons per uranium
ion in UO_2[13]. Now there is experimental evidence for some inter-
mediate valencies in metallic actinide compounds (see ref.[14]).
Unfortunately, the possibilities of a direct experimental
observation for such phenomena in these materials are quite
restricted. This is partly a result of the technological dif-
ficulties in obtaining pure single crystals of actinide ma-
terials, and partly a result of the difficulty in the theo-
retical interpretation of the experimental data which are ty-
pically more complex than in the case of the rare earths.

The experimental behaviour of the actinide materials strong-
ly depends on the strength of the spin-orbit coupling, crystal
field, Coulomb- and hybridization energies. All of them are
expected to be of the same importance in these compounds.
Therefore, considering these interactions, the same macrosco-
pic features can be explained by assuming different valen-
cies [14].

Reviewing the physical aspects discussed so far, we conclude
that there is no definitely known valence state in UO_2, as
also was shown in [21].

4. THEORETICAL INTERPRETATION

Valence transitions are induced by hybridization interac-
tions of 5f-states with conduction band states. These hybridi-
zation matrix elements strongly depend on the relative posi-
tion of the f-levels to the Fermi energy and the energy of the
different electronic configurations. The valence fluctuation
times also must show this dependence and one can predict dif-
ferent fluctuation times for each compound as well as for the
electrons in the different 5f-states. From the FWHM(see the
table) follow valence fluctuation times of an order of
$(10^{-13} - 10^{-14})$ sec.

For the theoretical interpretation of the experimental
neutron data in the "mixed valence" compound UO_2, we have to
make some assumptions. At present there are two different pos-
sibilities how to explain the ground state of an intermediate
valence compound.

The first assumes that the mixed valence system is a comp-
letely new many-particle system. Thus the ground state cannot
be explained by the ground states of the two individual valen-
cies being mixed. In this theory the ground state can be
described correctly only by the relativistic electron wave
functions of the solid taking into account hybridization in-
teractions and electron correlation effects.

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The second explanation neglects CEF contributions arising from hybridization interaction of the 5f-electrons with the conduction electrons. One can suggest the following simple physical picture. The energy level scheme of the CEF-splitted ground state multiplet can be obtained by a superposition of the two CEF-splitted ground states of the individual valencies. Penney and Holtzberg[15] proposed that the hybridization produces a localized mixed valence state, symbolically denoted by a linear combination of the two different valence configuration. For UO_2 one gets

$$\psi = A f^{(2)} d^{(1)} + B f^{(3)}.$$

Due to the valence fluctuations caused by hybridization interactions, the line width of the CEF levels increases drastically.

We now calculate the CEF splitting of the lowest-lying multiplets for the $5f^{(2)}$ and $5f^{(3)}$ configuration using the notations by Chan and Lam[3] including J—mixing effects of the excited multiplets to the ground state multiplet. The starting point for the determination of the splitting of the electronic multiplets in the CEF are free ion results taken from ref.[3]. The CEF-states $|\Gamma'\rangle$ are related to the Russel-Saunders basis set used to build up the Coulomb — and spin — orbit matrices by two successive unitary transformations.

$$|\Gamma'\rangle = \sum_{a, J} \langle a J|\Gamma'\rangle |a J\rangle, \tag{1}$$

with

$$|a J\rangle = \sum_{M_J} \langle a J M_J|a J\rangle |a J M_J\rangle$$

and

$$|a J M_J\rangle = \sum_{S,L} \langle 5f^{(n)} SLJM_J|a J M_J\rangle |5f^{(n)} SLJM_J\rangle.$$

The quantities a are the additional quantum numbers. Using the free ion multiplet energies E_0^J and the corresponding wave functions, tabulated in ref.[3] we get the following matrix equation for the determination of the CEF states

$$\sum_J \langle a J|\Gamma'\rangle \{H_{CEF}^{JJ'} + E_0^J \delta_{JJ'} - E \delta_{JJ'}\} \equiv 0. \tag{2}$$

The matrix elements $H_{CEF}^{JJ'} = \langle J|H_{CEF}|J'\rangle$ are given by a linear combination of matrix elements with the Russel-Saunders basis functions.

$$\langle 5f^{(n)} SLJM_J|H_{CEF}|5f^{(n)} S'L'J'M_J'\rangle. \tag{3}$$

The CEF splitting of the electronic multiplets for a given
$5f^{(n)}$ configuration can be described in good approximation
by the CEF Hamiltonian

$$H_{CEF} = \sum_{\ell=2,4,6} \sum_{m=-\ell}^{\ell} A_\ell^m \, Y_\ell^m \tag{4}$$

Y_ℓ^m are the spherical harmonics of the 5f electrons and A_ℓ^m
are CEF-parameters in a point charge model. In the standard
notations by Wybourne [16] the matrix elements of the Hamilto-
nian (4) can be written in the form

$$< 5f^{(n)} SLJM_J | H_{CEF} | 5f^{(n)} S'L'J'M_J' > = - \sum_{\ell,m} 7 A_\ell^m \, \delta_{SS'} \quad * $$

$$* \, (-1)^{m+S+L'+2J-M_J} \{(2J+1)(2J'+1)(2L+1)(2L'+1)\}^{1/2} * \tag{5}$$

$$* \begin{pmatrix} 3 & 3 & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & m & J' \\ -M_J & \ell & M_J' \end{Bmatrix} \begin{Bmatrix} L & J & S \\ J' & L' & m \end{Bmatrix} \quad * $$

$$* \, n \sum_{\bar{\psi}} (\psi | | \bar{\psi}) (\psi' | | \bar{\psi}) (-1)^{\bar{L}+m+3+L} \begin{Bmatrix} 3 & L & \bar{L} \\ L' & 3 & m \end{Bmatrix}$$

where the $(\psi | | \bar{\psi})$ are the fractional parentage coefficients. These
reduced matrix elements have been tabulated by Nielson and
Koster [17] for all the $f^{(n)}$ -configurations. All matrix elements
(5) can now be calculated for the two individual configura-
tions $5f^{(2)}$ and $5f^{(3)}$. Using the parametrization of Lea, Leask
and Wolf [18] for a cubic CEF, where only the A_ℓ^m with $\ell = 4,6$
and $m = 0 \pm 4$ are different from zero, we introduce the parameters
x,W. The parameter $x(-1 \leq x \leq 1)$ represents the ratio of fourth-
to sixth order parameters A_4^0 / A_6^0, and W is the scaling fac-
tor for the strength of CEF. From the diagonalization of mat-
rix equation (2) we find the energies of the CEF leves and
their wave functions in the two configurations adjusting the
CEF parameters x and W.

Now we try to find a set of CEF parameters and the confi-
guration number of f-electrons at the uranium ions in UO_2
which can theoretically explain the experimental data listed
in the table. For this purpose we assume that the CEF para-
meters in the two different configurations are the same.

From a fit to the experimental spectrum we find one set of
parameters x,W and a certain value for the number of 5f-elect-
rons per uranium ion. These values are

x = (0.65 ± 0.05); W = (4 ± 0.5) meV; $5f^{(2.35 \pm 0.05)}$.

The CEF splitting schemes of the two 5f-configurations as
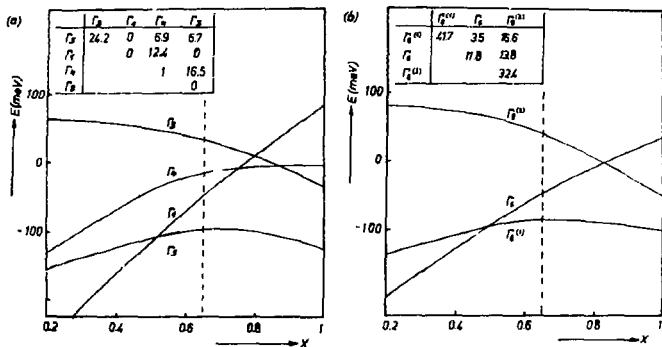a function of the parameter x (in this region) for W = 4 meV

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Fig.3. Splitting scheme of the ground state multiplet in dependence on the CEF parameter x for W=4 meV (a) $5f^{(2)}$ -configuration, (b) $5f^{(3)}$ -configuration. In the tables over the figures are given the corresponding transition probabilities at the fixed value of x=0.65.
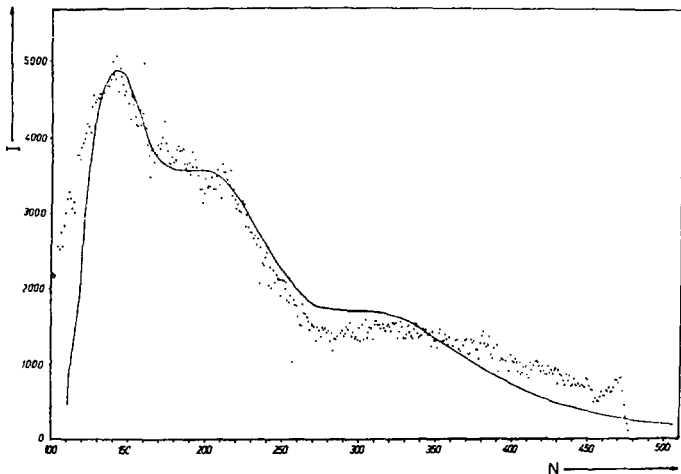

Fig.4. Theoretically reproduced magnetic neutron spectrum for UO_2 - full line, compared to the experimental data - points.

are shown in figure 3. The corresponding transition probabilities for the fixed value $x = 0.65$ are also given in figure 3. The theoretically reproduced spectrum compared to the experimental one is plotted in figure 4 (by the full line).

The very broad CEF-peaks in the experimental spectrum at energies 130, 80, 32 meV and the corresponding line-width of 70, 60, 33 meV qualitatively can be explained as follows.

Due to the hybridization interaction of the 5f-states with the conduction band states, the CEF levels are very strongly broadened. This cannot be explained by phonon scattering or by dynamical exchange effects. Also a collectivization of the 5f-electrons in small bands can be ruled out (see ref.[8]). The line-width of the transition peaks increases with increasing energy transfer. This fact is also in agreement with the predicted hybridization broadening because the excited CEF states lie closer to the Fermi energy and the hybridization interactions in these states are stronger than in the lower lying states.

The broad "peak" (distribution) in the low energy range of the spectrum is caused by quasielastic scattering of neutrons in the CEF ground state level. The width of this quasielastic line is of about 17.5 meV, which can be explained by valence fluctuations as proposed by Holland-Moritz[19] and Loewenhaupt et al.[20] and underlines our assumption of an intermediate valence state in UO_2.

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