JOURNAL OF SOLID STATE CHEMISTRY 87, 218–221 (1990)

AOM Reconciling of Crystal Field Parameters for UCl_3, UBr_3, UI_3 Series

Z. GAJEK AND J. MULAK

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wroclaw, P.O. Box 937, Poland

Received December 11, 1989; in revised form March 19, 1990

Available inelastic neutron scattering interpretations of crystal field effect in the uranium trihalides have been verified in terms of Angular Overlap Model. For UCl_3 a good reconciling of both INS and optical interpretations of crystal field effect has been obtained. On the contrary, the parameterizations for UBr_3 and UI_3 were found to be highly artificial and suggestion is given to experimentalists to reinterpret their INS spectra. © 1990 Academic Press, Inc.

Introduction

The proper interpretation of the Inelastic Neutron Scattering (INS) spectra for the U(3+) ion in the uranium trihalides (*1–5*) is crucial for understanding their intriguing magnetic properties at low temperatures (*3, 4, 6, 7*). The present discussion of the $^4I_{9/2}(5f^3)$ ground multiplet splitting along the homologous series is based upon the Angular Overlap Model (AOM). It reveals a large flexibility of the conventional crystal field model for various not necessary consistent interpretations of the INS data. Least-square's fittings of the AOM parameters to the observed energy spectra have been obtained within the simplified version of AOM including some inherent physical limitations of the model shown previously for the U(4+) compounds (*8*).

Crystal Structure and Crystal Field Parameterization

UCl_3 and UBr_3 are isostructural with $LaCl_3$, space group $P6_3/m$ (C_{6h}^2). The point symmetry of the uranium site is C_{3h}. Each U(3+) ion is coordinated with nine (6 + 3) nearly equidistant ligands arranged in the form of a tricapped trigonal prism.

UI_3 crystallizes with the orthorhombic $PuBr_3$-type structure, space group *Cmcm* (D_{2h}^{17}). The point symmetry of the uranium site is C_{2v}. The coordination polyhedron consists of eight (2 + 4 + 2) ligands lying at three slightly different distances (*6*).

In the all three compounds the U(3+) ion has the ground multiplet $^4I_{9/2}(5f^3)$, which is split into five Kramers doublets. For the C_{3h} point group (UCl_3, UBr_3) only the Γ_8–Γ_7 transition is magnetically forbidden whereas for the C_{2v} symmetry (UI_3) there are no restrictions.

The global parameterization of the crystal field potential (*9*),

$$V = \sum_i \sum_k \sum_q B_q^k C_q^k(i),$$

where i runs over all unpaired electrons, may often lead to several different interpretations of experimental splitting schemes. Some of them may be quite artificial, in par-

0022-4596/90 $3.00

ticular when the number of experimental observables is too small to determine the whole sets of the B_q^k parameters. In the present case there are four and nine B_q^k parameters for the C_{3h} and C_{2v} crystal field symmetries respectively and only two and three INS transitions observed. To make the problem tractable it is advisable to follow simplified models like the Newman's Superposition Model (SM) or the Angular Overlap Model. The parameters of the models, b_k for $k = 2$, 4, 6 and e_μ for $\mu = 0$ or σ, 1 or π, 2 or δ, respectively, describe the local interaction between an individual ligand and the central metal ion. The following relations apply (*10*),

$$b_k^l = \frac{2k+1}{2l+1}\left[\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}\right]^{-1} \sum_\mu (-1)^\mu (2 - \delta_{\mu 0}) \begin{pmatrix} l & k & l \\ -\mu & 0 & \mu \end{pmatrix} e_\mu^l$$

$$B_q^k = \sum_t C_q^{k*}(\Theta_t, \Phi_t) b_k^l$$

where Θ_t, Φ_t are the angular coordinates of t ligand in the main coordinate system, t runs over the ligands, and (: : :) denotes the $3-j$ symbol.

For f electrons ($l = 3$):

$$b_2 = \frac{5}{7}e_\sigma + \frac{15}{14}e_\pi$$

$$b_4 = \frac{9}{7}e_\sigma + \frac{3}{7}e_\pi - 3e_\delta$$

$$b_6 = \frac{13}{7}e_\sigma - \frac{39}{14}e_\pi + \frac{39}{35}e_\sigma.$$

The AOM parameters depend only on the distance between the interacting ions and take the values from the ranges specified for each metal–ligand system. Additionally, they are naturally ordered: $e_\sigma > e_\pi > |e_\delta|$ (e_δ in contrast to e_σ and e_π may be negative) and may be well predicted from the overlap contribution only (*10*). In the present calculations the squares of the respective interionic overlap integrals have been used to estimate the $e_\pi : e_\sigma$ ratio and the dependence of e_σ and e_π on metal–ligand distance. The distance dependence of the e_δ parameter has been obtained from ab initio calculations described in Ref. (*10*). The resulting two-parameter (e_σ, e_δ) effective model has been applied to reinterpret observed INS transitions using the standard least-square's fitting procedure.

Results

UCl_3. There are two sources of information about the substructure of the split $^4I_{9/2}$ multiplet in UCl_3: INS (*3*, *4*) and optical spectroscopy (*11*). In the INS spectrum one observes two transitions at 34 and 57 meV. Independently, the system of the five lowest doublets of the $^4I_{9/2}$ multiplet was deduced from fluorescence transitions directly involving the components of the ground state for U^{3+} : $LaCl_3$ (*11*) (Table I).

The parameters e_μ, b_k, and B_q^k corresponding to column (i) of Table I are presented in Table IV.

UBr_3. Two strong and rather wide peaks at about 26 and 44 meV were found on INS spectrum of UBr_3 (*1*, *2*, *4*). The position of the invisible Γ_7 doublet is the key problem in the interpretation. In the original paper it

TABLE I

ENERGY PATTERNS (meV) OF SPLIT $^4I_{9/2}$ MULTIPLET IN UCl_3 CALCULATED ON THE GROUND OF INS DATA (*3*, *4*)—(i), AND DEDUCED FROM FLUORESCING TRANSITIONS FOR U^{3+} : $LaCl_3$ (*11*)—(ii)

Level	(i)	(ii)
$\Gamma_8^{(1)}$	0	0
Γ_7	32	26
$\Gamma_9^{(1)}$	34	30
$\Gamma_8^{(2)}$	57	55
$\Gamma_9^{(2)}$	60	56

TABLE II

ENERGY PATTERNS (meV) OF SPLIT $^4I_{9/2}$ MULTIPLET IN UBr_3

Level	INS[a]	*a*	*b*	*c*
$\Gamma_8^{(1)}$	0	0	0	0
Γ_7	(2.5)[b]	5.3	26.6	23.7
$\Gamma_9^{(1)}$	26.6	21.1	26.3	24.9
$\Gamma_8^{(2)}$	41.9	43.0	41.7	45.4
$\Gamma_9^{(2)}$	45.7	46.7	46.0	48.5

Note. *a*, fitting for Γ_7 at 2.5 meV; *b*, fitting for unfixed Γ_7; *c*, fluorescence transitions observed for $U^{3+}:LaBr_3$ (*12*).

[a] Refs. (*1*, *2*, and *4*).

[b] Hypothetical value estimated from difference of transitions.

was placed near the ground Γ_8 doublet. The best AOM fitting for this pattern is presented in column *a* of Table II. Column *b* presents another fitting to the same experimental scheme, but without fixing the Γ_7 position. The latter result turns out to be consistent with the independent data deduced from fluorescence transitions for $U^{3+}:LaBr_3$ by Paszek (*12*).

The two sets of the e_μ, b_k, and B_q^k parameters corresponding to columns *a* and *b* are presented in Table IV.

UI_3. The results obtained for this compound are a good verification of our AOM test; despite different crystal structure, the b_k and e_μ parameters should be in line with those for the trichloride and tribromide. Some spectrochemical shift is obviously expected. For UI_3 three peaks at 15.5, 25.0, and 37.0 meV have been observed (*5*). The position of one Kramers doublet is undetermined. In the original paper it was fixed near the ground level. The corresponding best AOM fitting is shown in column *a* of Table III. We propose another fitting, column *b*, with pseudo-degenerate 37 meV level.

It was checked numerically that there are no other realistic patterns. The e_μ, b_k, and B_q^k parameters corresponding to the two variants are compiled in Table IV.

TABLE III

ENERGY PATTERNS (meV) OF SPLIT $^4I_{9/2}$ MULTIPLET IN UI_3

Level	Experiment	*a*	*b*
(1) (1)	0	0	0
(2)		1.9	
(3) (2)	15.5	16.2	16.8
(4) (3)	25.0	25.5	26.0
(5) (4)	37.0	36.0	35.3
(5)			37.2

Note. *a*, fitting for degeneration of (1) and (2) levels; *b*, fitting for degeneration of (4) and (5) levels.

TABLE IV

e_μ, b_k, and $B_q^{(k)}$ PARAMETERS OF U(3+) ION IN UX_3 COMPOUNDS (meV)[a]

		UBr_3		UI_3		
	UCl_3	*a*	*b*	*a*	*b*	ab initio U–Br[b]
e_σ	74	−92	57	13.8	57.2	83
e_π	28	−107	22	−15.9	20.6	31
e_δ	4	−57	3	8.6	7.8	0.9
b_2	84	−180	64	−7.1	63.0	92
b_4	97	8	74	−14.8	59.0	117
b_6	63	61	49	79.5	58.0	70
B_0^2	44	−96	33	3.8	−10.1	
B_0^4	−113	−32	−106	3.8	−13.1	
B_0^6	−154	−131	−106	3.3	3.3	
B_6^{6c}	105	92	81	17.5	13.5	
B_2^2				2.1	−16.3	
B_2^4				2.9	0.7	
B_4^4				35.0	−116.7	
B_2^6				89.6	69.6	
B_4^6				−35.8	−27.5	

Note. *a*, original interpretation; *b*, new interpretation.

[a] meV ≈ 8 cm^{-1} ≈ 12 K.

[b] Calculations based on the perturbative model described in Ref. (*10*).

[c] The sign for C_{3h} point group is inessential.

Discussion

The main feature seen from the summary Table IV is the convincing regularity of both b_k and e_μ parameters found for UCl_3 and

the patterns (*b*) in contrast to self-evident divergence for the patterns (*a*). This is just the AOM test. In the latter case the negative sign some of e_μ and b_k parameters is a particular symptom of their fictitious character. For comparison, the results of almost complete ab initio calculations (except polarization contributions) of b_k and e_μ performed for the U–Br binary system of 3.13-Å interionic distance are also shown in Table IV. Their values and mutual hierarchy are consistent with those found in our interpretations. A small value for e_δ is additional evidence of physical correctness of the approach.

Table IV reflects the anticipated decrease of the crystal field strength along the UX_3 series. The results for UCl_3 are consistent with the known interpretation of the optical spectrum of $U(3+):LaCl_3$ (*11*) and the data extrapolated from the $NdCl_3$ study (*13*). They also confirm the original INS interpretation by Murasik *et al.* (*3, 4*). Unfortunately, in the case of the two remaining homologous compounds the interpretation given by Murasik *et al.* (*4, 5*) is not to be reconciled with the AOM approach. The latter excludes the energy level lying below 10 meV for both UBr_3 and UI_3. Since the INS interpretation seems to be, from the AOM point of view, definitely artificial it is recommended that experimentalists look for a new interpretation consistent for UX_3 series.

Acknowledgments

We are indebted to Dr. A. Murasik for providing the data for UI_3 prior to the publication and to Dr. R. Łyżwa for inspiring discussions. We quoted the $U^{3+}:LaBr_3$ data from the Ph.D. dissertation by A. P. Paszek due to the courtesy of one of reviewers.

References

1. A. Murasik and A. Furrer, *Physica B* **102,** 185 (1980).
2. A. Murasik, A. Furrer, and W. Szczepaniak, *Solid State Commun.* **33,** 1217 (1980).
3. A. Murasik, P. Fischer, A. Furrer, and W. Szczepaniak, *J. Phys. C: Solid State Phys.* **18,** 2909 (1985).
4. A. Murasik, P. Fischer, A. Furrer, and B. Schmid, *J. Less-Common Met.* **121,** 151 (1986).
5. A. Murasik, A. Furrer, P. Fisher, and W. Szczepaniak, 17emes Journees des Actinides, Chextres, Switzerland 1987, Abstract Booklet, p. 55.
6. A. Murasik, P. Fischer, and W. Szczepaniak, *J. Phys. C: Solid State Phys.* **14,** 1847 (1981).
7. R. Łyżwa and P. Erdös, *Phys. Rev. B* **36,** 8570 (1987).
8. Z. Gajek, S. Hubert, and J. C. Krupa, *J. Magn. Magn. Mat.* **76/77,** 363 (1988).
9. B. G. Wybourne, "Spectroscopic Properties of Rare Earths," Wiley, New York (1965).
10. Z. Gajek, J. Mulak, and M. Faucher, *J. Phys. Chem. Solids* **48,** 947 (1987).
11. H. M. Crosswhite, H. Crosswhite, W. T. Carnall, and A. P. Paszek, *J. Chem. Phys.* **72,** 5103 (1980).
12. A. P. Paszek, Ph.D. dissertation, Johns Hopkins University, Baltimore, Maryland, 1978.
13. E. Y. Wong, *J. Chem. Phys.* **34,** 1989 (1961).