Title

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Author

Edelstein, N.

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N. Edelstein and D. Karraker

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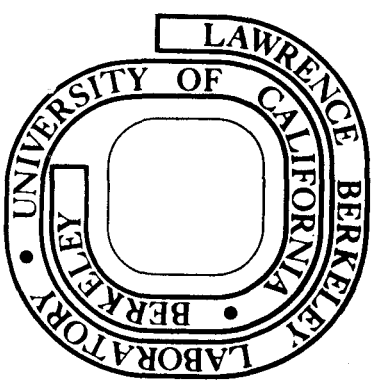

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Comment on "Electronic Structure of UF_6^-"

by M. Boring, J. H. Wood, and J. W. Moskowitz
J. Chem. Phys. 61, 3800 (1974)

by

N. Edelstein

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

D. Karraker

E. I. duPont de Nemours & Co., Inc.
Savannah River Laboratory
Aiken, South Carolina 29801

In a recent paper Boring, Wood, and Moskowitz report the results of a non-relativistic SCF-Xα - scattered wave calculation on the UF_6^- ion. They compare their calculated orbital energy levels with experimental data published on this ion by Reisfeld and Crosby.[2] We wish to point out the assignments of Reisfeld and Crosby have been questioned and it is now generally agreed some aspects of their analysis were incorrect.[3-7] Furthermore, a straightforward analysis of the optical and magnetic data for this ion based on the crystal field model allows a determination of the 5f orbital energies for a direct comparison with the results of the Xα calculation.[7] The results of such an analysis are shown in Table I. However, if the orbital reduction factors are included in the analysis the 5f orbital energies derived from the data will shift markedly.[8] At this time there have been no unambiguous determinations of the orbital reduction factors.

The main conclusions (based upon their calculation and its approximations) of Boring, Wood, and Moskowitz are valid. Our objection to their paper is the use of data which has been shown to be incorrect.

References

1. M. Boring, J. H. Wood, and J. W. Moskowitz, J. Chem. Phys. 61, 3800 (1974).
2. M. J. Reisfeld and G. A. Crosby, Inorg. Chem. 4, 65 (1965).
3. J. L. Ryan, "MTP International Review of Science, Inorganic Chemistry Series One", K. W. Bagnall, Editor (Butterworths, London, 1972), p. 332.
4. C. J. Ballhausen, Theoret. Chem. Acta (Berl) 24, 234 (1972).
5. J. Selbin, C. J. Ballhausen, and D. G. Durrett, Inorg. Chem. 11, 510 (1972).
6. J. Ryan, J. Inorg. Nucl. Chem. 33, 153 (1971).
7. N. Edelstein, D. Brown, and B. Whittaker, Inorg. Chem. 13, 563 (1974).
8. N. Edelstein, unpublished results.

Table I. Results of a crystal field analysis on UF_6^-.

$\Gamma_7 - \Gamma_6$	$\Gamma_7 - \Gamma_8'$	$\Gamma_7 - \Gamma_7'$	θ	Δ	ψ
(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
15900[a]	13715[a]	7413[a]	6882[b]	4479[b]	1885[b]
			13718[c]	4057[c]	

[a] Experimental assignments from Ref. 6.

[b] Results of the crystal field analysis from Ref. 7. Nomenclature as in this reference.

[c] Results of the SCF Xα calculation from Ref. 1.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720