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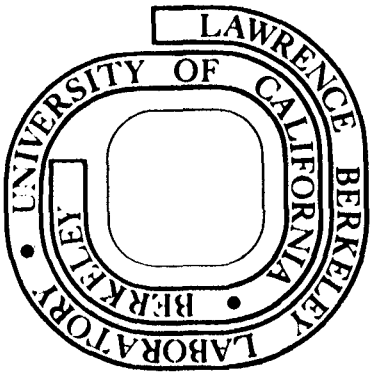

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Covalency in Octahedrally Coordinated $5f^1$ Complexes

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Summary. — The application of crystal field and molecular orbital theory to an octahedrally coordinated f^1 system is reviewed. The optical and magnetic data available for UX_6^- (X = F, Cl, Br) complexes are analyzed in terms of these theories. We show the usual approximation for the orbital reduction factors, $k_{a_2t_2} = \sqrt{k_{t_2t_2}}$, is not meaningful for UX_6^- (X = Cl, Br). We evaluate qualitatively the orbital reduction factors $k_{a_2t_2}$ and $k_{t_2t_2}$ for each UX_6^- complex and show their values correlate with an increase in covalency in the UX_6^- complexes as X changes from F to Br.

Introduction

Lanthanide compounds are generally regarded as ionic in character because the 4f electron shell does not have a significant spatial extent and is shielded from the ligand environment by the filled $5p^6 6s^2$ shells. The 5f electron shell does have a considerable spatial extent, especially at the beginning of the actinide series, and compounds of the f transition series may be characterized by covalent bonding. Experimental evidence supports this contention. The early actinide metals have properties which are more similar to d-transition series metals rather than 4f metals because of 5f electron hybridization.[1] The stability of

cyclooctatetraene complexes of the tetrapositive actinide ions has been attributed to 5f orbital covalency.[2] Direct evidence for covalent interactions in 5f compounds comes from the observation of superhyperfine structure in the electron paramagnetic resonance (epr) spectra of NpF_6,[3] and U^{3+} and Pu^{3+} diluted in CaF_2.[4-5]

Recently we have qualitatively interpreted the magnetic resonance and optical spectra of $5f^1$ hexahalide complexes in terms of molecular orbital theory.[6] In this paper we review the application of molecular orbital theory to $5f^1$ octahedral complexes [7-11] and then apply it to the data available for U^{5+} hexahalide compounds.

Review of Theory

The crystal field model for octahedral symmetry considers six point charges, each placed at an equal distance from the origin on three mutually perpendicular axes. There are seven f orbitals which split into two triplets and one singlet (not including the spin degeneracy) in this symmetry. The orbital wavefunctions and symmetry labels are given in Table I. The a_{2u} orbital (singlet) points toward the corners of a cube and is furthest from the negatively charged ligands so is lowest in energy; the t_{2u} orbitals (triplet) point toward the centers of the edges of the cube and are next lowest in energy; while the t_{1u} orbitals (triplet) point directly at the ligands and are highest in energy.[12]

The molecular orbital model requires the linear combination of the ligands of the proper symmetry to mix with the metal f orbitals. If we consider only the s and p orbitals on the ligands, then we find

the a_{2u} orbital is nonbonding, the t_{2u} orbitals are π bonding, and the t_{1u} orbitals are σ and π bonding. Fig. 1 defines the coordinate system for the octahedral complex. The metal ion is at the center and two ligands each at a distance a from the origin are on three mutually perpendicular axes. The molecular orbital wavefunctions are given in Table II.[7,8]

Crystal Field Model

The Hamiltonian for a f electron in octahedral symmetry is

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{SO} + \mathcal{H}_{CF} \\ \mathcal{H}_{SO} &= \zeta(r)\ \vec{\ell}_i \cdot \vec{s}_i \\ \mathcal{H}_{CF} &= B_0^4[C_0^{(4)} + \sqrt{5/14}\ (C_{-4}^{(4)} + C_4^{(4)})] \\ &\quad + B_0^6[C_0^{(6)} - \sqrt{7/2}\ (C_{-4}^{(6)} + C_4^{(6)})] \end{aligned} \tag{1}$$

where $\zeta(r)$ (from now written as ζ) is the spin-orbit coupling constant, and B_0^4 and B_0^6 are the crystal field parameters.[13,14] The spin and orbital angular momentum operators, $\vec{s}_i$ and $\vec{\ell}_i$, and the $C_q^{(k)}$, the tensor operators used to describe the crystal field, depend only on the angular coordinates, and are readily evaluated.

The energy level diagram obtained from the above Hamiltonian (for the special case $B_0^6 = 0$) is shown in Fig. 2. The left hand side of the figure shows the limit of the strong crystal ($V_{CF} \gg V_{SO}$) while the right-hand side shows the strong spin-orbit coupling limit ($V_{SO} \gg V_{CF}$). The splittings of the f orbitals in a strong crystal field may be

represented by two parameters Θ and Δ which are related to the parameters B_0^4 and B_0^6 of equation 1 by

$$b_4 = B_0^4/33 \quad , \quad b_6 = -\sqrt{5/429}\, B_0^6$$
$$\Theta = 8b_4 - 56b_6 \tag{2}$$
$$\Delta = 10b_4 + 84b_6 \quad .$$

If the strong crystal field states are used as the basis states the energy matrices are

$$\Gamma_7: \begin{vmatrix} 0 & \sqrt{3}\zeta \\ \sqrt{3}\zeta & \Delta - \frac{1}{2}\zeta \end{vmatrix}$$

$$\Gamma_8: \begin{vmatrix} \Delta + \frac{1}{4}\zeta & \frac{3}{4}\sqrt{5}\zeta \\ \frac{3}{4}\sqrt{5}\zeta & \Delta + \Theta - \frac{3}{4}\zeta \end{vmatrix} \tag{3}$$

$$\Gamma_6: \begin{vmatrix} \Delta + \Theta + \frac{3}{2}\zeta \end{vmatrix}$$

The g value for the ground Γ_7 state is

$$g_{\Gamma_7} = 2\cos^2\alpha - \frac{8}{\sqrt{3}}\sin\alpha\cos\alpha \tag{4}$$

and

$$\tan 2\alpha = \frac{2\sqrt{3}\zeta}{\Delta - \frac{1}{2}\zeta} \quad , \quad E_{\Gamma_7'} - E_{\Gamma_7} = \frac{2\sqrt{3}\zeta}{\sin 2\alpha} \quad . \tag{5}$$

Molecular Orbital Theory

The f orbital wavefunctions and the proper linear combination of ligand orbitals were given in Table II. The normalization factors, N and N' are given by [8]

$$N^2 = (1 - 4\alpha_\pi S_\pi - 2\sqrt{2}\,\alpha_\sigma S_\sigma - 2\sqrt{2}\,\alpha_s S_s + \alpha_\pi^2 + \alpha_\sigma^2 + \alpha_s^2)^{-1}$$

$$N'^2 = (1 - 4\alpha'_\pi S'_\pi + \alpha'^2_\pi)^{-1} \qquad (6)$$

The overlap integrals are

$$S_\pi = \langle f_x | -x_3 \rangle \quad , \quad S_\sigma = \langle f_x | -x_1 \rangle \quad ; \quad S_s = \langle f_x | s_1 \rangle \quad ;$$

$$S'_\pi = \langle f_\xi | -x_3 \rangle \quad . \qquad (7)$$

The magnitudes of the admixture coefficients α_π, α_σ, α_σ, and α'_π represent the amount of ligand character mixed into the metal ion orbitals.

The orbital angular momentum reduction factors k_{ij} are defined by

$$k_{ij} = \frac{\langle f'_i | \vec{\ell} | f'_j \rangle}{\langle f_i | \vec{\ell} | f_j \rangle} \qquad (8)$$

The functions used in the numerator of equation 8 are the molecular orbitals of Table II while the functions of the denominator are the pure ionic parameters.

For octahedral symmetry there are four orbital reduction factors, $k_{t_1t_1}$, $k_{t_2t_2}$, $k_{a_2t_2}$, and $k_{t_1t_2}$. Thornley [8] has given the explicit expressions for these parameters (assuming α and α' are small and N and N' are close to 1):

$$k_{t_1t_1} = 1-N^2\{\frac{1}{3}\,4\alpha_\pi^{\,2} + \alpha_\sigma^{\,2} + \alpha_s^{\,2} + (\frac{2\sqrt{2}}{3})\alpha_\pi(\alpha_\sigma + a\alpha_s < x|\frac{\delta}{\delta x}|s>)\}$$

$$k_{t_2t_2} = 1-2N'^2\,\alpha_\pi'^2$$

$$k_{a_2t_2} = 1-\frac{1}{2}N'\alpha_\pi'^2$$

$$k_{t_1t_2} = 1-NN'\{\frac{1}{2}(\alpha_\pi^{\,2} + \alpha_\pi'^2 + \alpha_\sigma^{\,2} + \alpha_s^{\,2}) + \sqrt{2/15}(\alpha_\sigma\alpha_\pi' - \frac{\alpha_\pi\alpha_\pi'}{\sqrt{2}}$$

$$+ \alpha_s\alpha_\pi'\, a < x|\frac{\delta}{\delta x}|s)\} \quad . \tag{9}$$

For a further discussion of these expressions see Thornley [8] and Owen Thornley.[15]

The energy matrices of equation 3 are now modified by replacing by the appropriate $k_{ij}\,\vec{\ell}$ and assuming $\zeta(r)$ is the free ion spin-orbit coupling constant. The energy matrices are now:

$$\Gamma_7: \begin{vmatrix} 0 & \sqrt{3}\,k_{a_2t_2}\zeta \\ \sqrt{3}\,k_{a_2t_2}\zeta & \Delta - \frac{1}{2}k_{t_2t_2}\zeta \end{vmatrix}$$

$$\Gamma_8: \begin{vmatrix} \Delta + \frac{1}{4}\,k_{t_2t_2}\zeta & \frac{3}{4}\sqrt{5}\,k_{t_1t_2}\zeta \\ \frac{3}{4}\sqrt{5}\,k_{t_1t_2}\zeta & \Delta + \Theta - \frac{3}{4}\,k_{t_1t_1}\zeta \end{vmatrix} \tag{10}$$

$$\Gamma_6: \begin{vmatrix} \Delta + \Theta + \frac{3}{2}\,k_{t_1t_1}\zeta \end{vmatrix}$$

The g value for the ground Γ_7 state is

$$g_{\Gamma_7} = 2\cos^2\alpha - \frac{8}{\sqrt{3}} k_{a_2t_2} \sin\alpha\cos\alpha + \frac{2}{3}(k_{t_2t_2}-1)\sin^2\alpha \qquad (11)$$

and for the excited Γ_7' state

$$g_{\Gamma_7'} = 2\sin^2\alpha + \frac{8}{\sqrt{3}} k_{a_2t_2} \sin\alpha\cos\alpha + \frac{2}{3}(k_{t_2t_2}-1)\cos^2\alpha \quad , \qquad (12)$$

and

$$\tan 2\alpha = \frac{2\sqrt{3}\, k_{a_2t_2}\zeta}{\Delta - \frac{1}{2} k_{t_2t_2}\zeta} \quad . \qquad (13)$$

One can easily show that

$$E_{\Gamma_7'} - E_{\Gamma_7} = \frac{2\sqrt{3}\, k_{a_2t_2}\zeta}{\sin 2\alpha} \qquad (14)$$

When $k_{a_2t_2} = k_{t_2t_2} = k_{t_1t_1} = k_{t_1t_2} = 1$, these equations reduce to those given earlier for the ionic crystal field model.

Experimental Results and Interpretation

Spectral data on NpF_6, UX_6^- (X = F, Cl, Br) and PaX_6^{2-} (X = F, Cl, Br, I) have been published. [16,17,18] In addition there are electron paramagnetic resonance (epr) measurements on NpF_6, the UX_6^- compounds, and $PaCl_6^{2-}$.[16] The optical spectra are dominated by vibronic bands but the electronic bands have been assigned on the basis of the energy level diagram shown in Fig. 2 with

$$\frac{\frac{7}{2}\zeta/18b_4}{1 + \frac{7}{2}\zeta/18b_4} \sim .5 \quad .$$

One of the sharpest features in the spectra is the line assigned to the $\Gamma_7 \rightarrow \Gamma_7'$ transition. This transition is most likely of magnetic dipole origin which would account for its narrow linewidth. Its energy can be accurately measured and together with the ground state g value allows us to use equations 4 and 5 to obtain accurate values for the parameters ζ and Δ based on the simple crystal field theory. Since the most complete data is available for the UX_6^- compounds we shall use only this series. Table III gives the results. We see that ζ is fairly constant for all three complexes but Δ, which depends only on π bonding, decreases markedly as the ligand changes from F^- to Br^-.

Now let us consider the same data but apply the molecular orbital theory. In this case we use the free ion value of ζ which has been calculated from relativistic wavefunctions to be $\zeta = 2172cm^{-1}$ for U^{5+}, and by comparison with the available experimental data has been estimated to be accurate to $\pm 50cm^{-1}$.[9,19] From equations 11, 13, and 14 we can evaluate the three parameters, $k_{a_2t_2}$, $k_{t_2t_2}$, and Δ_{MO}. The approximation $k_{a_2t_2} = \sqrt{k_{t_2t_2}}$ was made by Eisenstein and Pryce and by Hecht, et al.[9,10] We make the same approximation and note from equation 14 that

$$\sin 2\alpha = \frac{2\sqrt{3}\, k_{a_2t_2}\, \zeta}{E_{\Gamma_7'} - E_{\Gamma_7}} \leq 1 \quad . \tag{15}$$

The results are given in Table IV.

With the experimental data, the calculated free ion spin-orbit coupling constant ζ, and the above approximation, it is impossible to fit the experimental data for UCl_6^{2-} and UBr_6^{2-}. We conclude the approximation $k_{a_2t_2} = \sqrt{k_{t_2t_2}}$ is not valid.

The next step is to allow $k_{a_2t_2}$ and $k_{t_2t_2}$ to be independent. However, we do not have enough experimental data to unambiguously fit $k_{a_2t_2}$ and $k_{t_2t_2}$ for each of the three complexes. We assume that $k_{a_2t_2}$ and $k_{t_2t_2}$ will be close to 1 and find the maximum values for each parameter which will fit the experimental data. This procedure at the very least will provide the trends in the orbital reduction factors as the halide is varied. The results are shown in Table V.

First of all, we are able to fit the data for the three UX_6^- complexes with this model. Secondly, the value of $k_{a_2t_2}$ appears almost constant for the three complexes although $k_{t_2t_2}$ changes markedly. However, as shown in Fig. 3, small changes in the value of $k_{a_2t_2}$ can drastically affect the value of $k_{t_2t_2}$. Qualitatively, the results follow the expected pattern. The orbital reduction factors are smaller (more covalent bonding) for the less electronegative ligands, i.e., the U^{5+} - Br^- bond is more covalent than the U^{5+} - F^- bond. Thirdly, the value of the ligand field parameter Δ is strongly affected by the values of $k_{a_2t_2}$ and $k_{t_2t_2}$; for the UCl_6^- and UBr_6^- complexes this parameter is approximately half the magnitude as found with the crystal field theory (see Table III).

Finally, we wish to point out that the values of $k_{a_2t_2}$ and $k_{t_2t_2}$ can be determined unambiguously. Equation 12 shows the g value for

the excited Γ_7' state which also depends on $k_{a_2t_2}$ and $k_{t_2t_2}$. The measurement of this quantity will allow us to unambiguously determine the orbital reduction factors. Table VI shows the calculated values of $g_{\Gamma_7'}$ for the UX_6^- complexes based on the data previously given for the crystal field model and the molecular orbital model. Essentially the deviations of the sum of g_{Γ_7} and $g_{\Gamma_7'}$ from 2.00 will be due to the orbital reduction factors (see equations 11 and 12).

Other mechanisms which we have not considered here such as the orbit-lattice interaction [20] or the Jahn-Teller effect [21] could also cause lowering of the g values. B. R. Judd [22] has recently shown the Jahn-Teller effect will not provide a plausible explanation for the low values of $k_{t_2t_2}$ for the UCl_6^- and UBr_6^- complexes found in this work. The experimental measurement of $k_{t_2t_2}$ should provide the impetus for further theoretical studies.

Acknowledgments

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Orbital	Representation
$f_{a_2} = \left(\frac{105}{4\pi}\right)^{\frac{1}{2}} xyz/r^3$	a_{2u}
$f_x = \left(\frac{7}{16\pi}\right)^{\frac{1}{2}} (5x^3-3xr^2)/r^3$	t_{1u}
$f_y = \left(\frac{7}{16\pi}\right)^{\frac{1}{2}} (5y^3-3yr^2)/r^3$	t_{1u}
$f_z = \left(\frac{7}{16\pi}\right)^{\frac{1}{2}} (5z^3-3zr^2)/r^3$	t_{1u}
$f_\xi = \left(\frac{105}{16\pi}\right)^{\frac{1}{2}} x(y^2-z^2)/r^3$	t_{2u}
$f_\eta = \left(\frac{105}{16\pi}\right)^{\frac{1}{2}} y(z^2-x^2)/r^3$	t_{2u}
$f_\zeta = \left(\frac{105}{16\pi}\right)^{\frac{1}{2}} z(x^2-y^2)/r^3$	t_{2u}

Table I. f orbitals in octahedral symmetry

Orbital	Representation
$f'_{a_2} = f_{a_2}$	a_{2u}
$f'_x = N\{f_x - 1/2\,\alpha_\pi\,(-x_3-x_6-x_2-x_5) - \sqrt{1/2}\,\alpha_\sigma(-x_1-x_4) - \sqrt{1/2}\,\alpha_s\,(s_1-s_4)\}$	t_{1u}
$f'_y = N\{f_y - 1/2\alpha_\pi(-y_1-y_4-y_3-y_6) - \sqrt{1/2}\,\alpha_\sigma\,(-y_2-y_5) - \sqrt{1/2}\,\alpha_s\,(s_2-s_5)\}$	t_{1u}
$f'_z = N\{f_z - 1/2\,\alpha_\pi\,(-z_2-z_5-z_1-z_4) - \sqrt{1/2}\,\alpha_\sigma\,(-z_3-z_6) - \sqrt{1/2}\,\alpha_s\,(s_3-s_6)\}$	t_{1u}
$f'_\xi = N'\{f_\xi - 1/2\alpha'_\pi(-x_3-x_6+x_2+x_5)\}$	t_{2u}
$f'_\eta = N'\{f_\eta - 1/2\alpha'_\pi(-y_1-y_4+y_3+y_6)\}$	t_{2u}
$f'_\zeta = N'\{f_\zeta - 1/2\alpha'_\pi(-z_2-z_5+z_1+z_4)\}$	t_{2u}

Table II. Molecular orbital wavefunctions in octahedral symmetry. The x_i, y_i, z_i labels refer to the p orbitals on each of the i ligands, the s_i refers to the s orbitals on each of the i ligands (i = 1-6). N and N' are normalization parameters. (After Thornley)

Compound	g_{exp}[a]	$E_{\Gamma_7-\Gamma'_7}$ (cm^{-1})	ζ (cm^{-1})	Δ (cm^{-1})
UF_6^-	-.748	7413	1970	3882
UCl_6^-	(-)1.12	6801	1938	2056
UBr_6^-	(-)1.21	6823	1961	1623

[a] Parentheses indicate the sign of the g value is not measured.

Table III. Values of ζ and Δ obtained from crystal field theory.

Compound	$\Gamma_7-\Gamma_7'$ (cm^{-1})	g_{exp}	g_{calc}	$k_{t_2t_2}$
UF_6^-	7413	-.748	-.747	.870
UCl_6^-	6801	(-)1.12	——	——
UBr_6^-	6823	(-)1.21	——	——

Table IV. Values of $k_{t_2t_2}$ with the approximation $k_{a_2t_2} = \sqrt{k_{t_2t_2}}$, $\zeta = 2172\ cm^{-1}$.

Compound	$E_{\Gamma_7-\Gamma_7'}$ (cm^{-1})	g_{exp}	g_{calc}	$k_{a_2t_2}$	$k_{t_2t_2}$	Δ calc (cm^{-1})
UF_6^-	7413	-.748	-.745	.935	.95	3369
UCl_6^-	6801	(-)1.12	-1.12	.903	.75	1119
UBr_6^-	6823	(-)1.21	-1.21	.906	.50	835

Table V. Maximum values of $k_{a_2t_2}$ and $k_{t_2t_2}$ obtained with ζ = 2172 cm^{-1}.

Compound	g_{Γ_7} exp	C.F. $g_{\Gamma_7'}$ calc	M.O. $g_{\Gamma_7'}$ calc
UF_6^-	-.748	2.748	2.72
UCl_6^-	-1.12	3.12	2.95
UBr_6^-	-1.21	3.21	2.88

Table VI. Calculated values of $g_{\Gamma_7'}$ using the crystal field model and the molecular orbital theory.

Figure Captions

Fig. 1. Coordinate system for an octahedral complex (after Thornley). (XBL769-3931)

Fig. 2. Energy level diagram for an f^1 system (Assuming $B_0^6 = 0$). (XBL743-513)

Fig. 3. Values of $k_{a_2t_2}$ and $k_{t_2t_2}$ (full line) which will fit g_{exp} for the Γ_7 state of UF_6^-. The variation of Δ (dashed line) with $k_{a_2t_2}$ is also given. The data from Table V are used for this figure. (XBL769-3930)

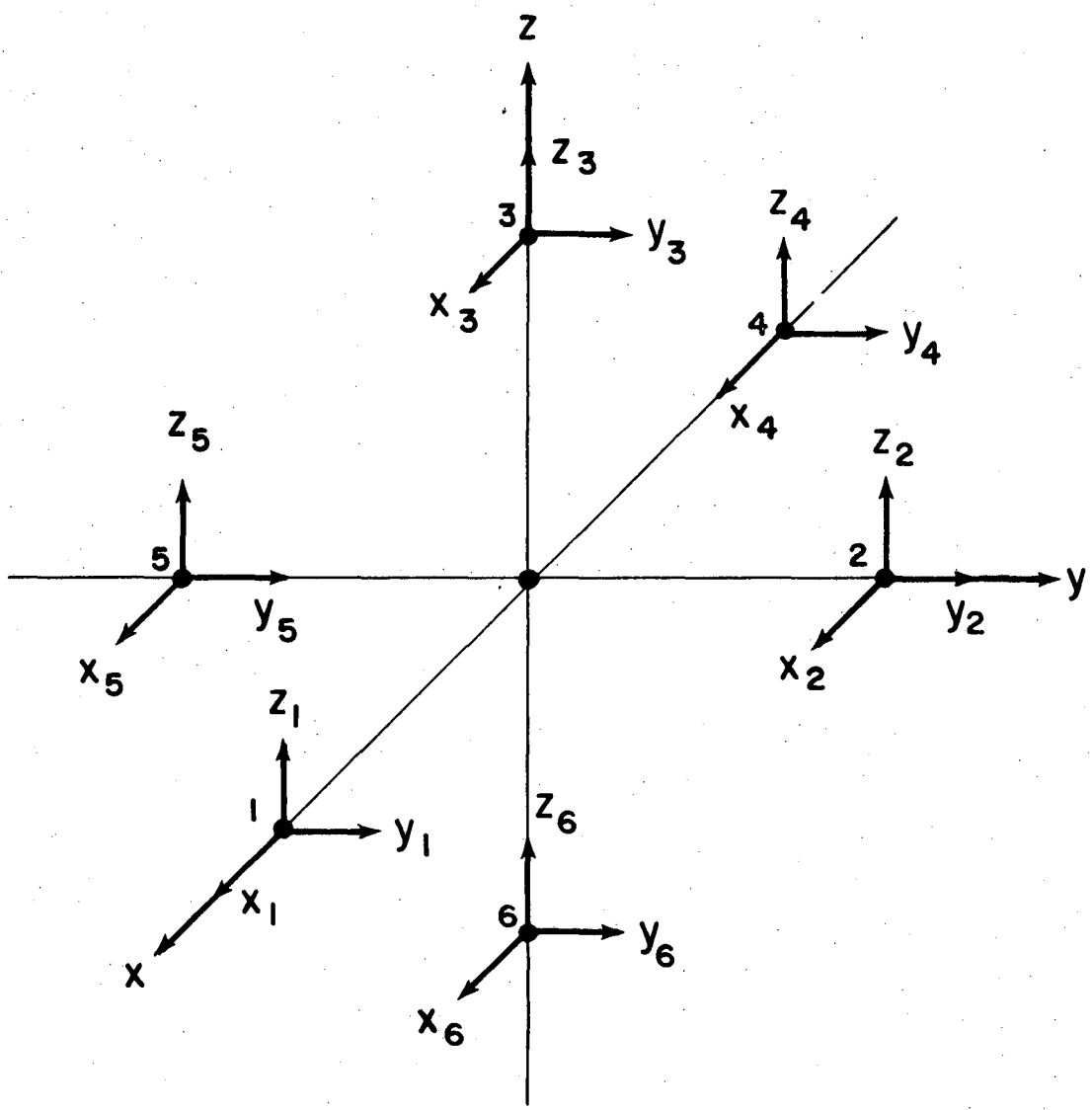
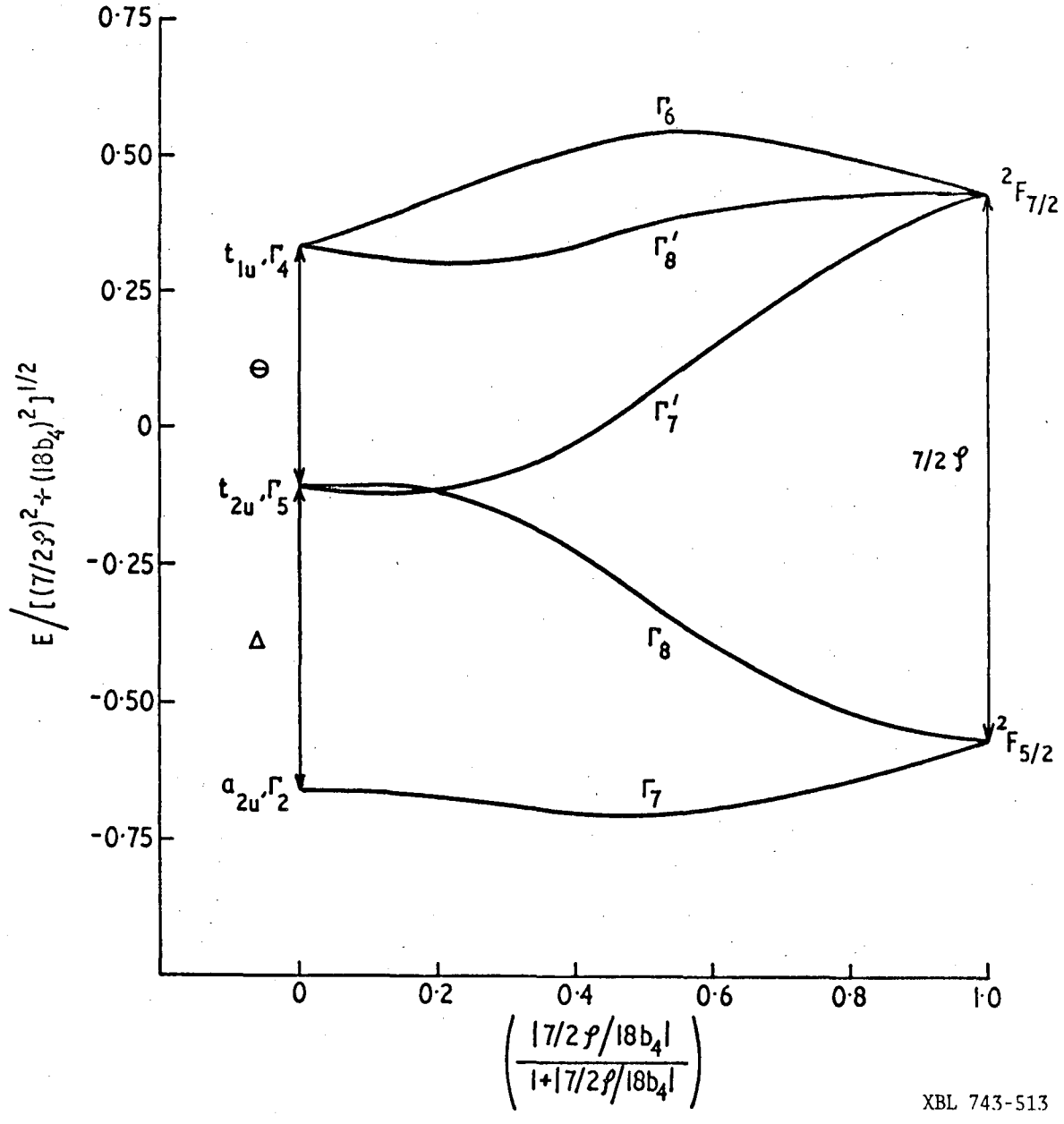


Fig. 1

XBL 769-3931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Γ_8'
Θ
Γ_7'
$7/2\,\zeta$
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Δ
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$^2F_{5/2}$
a_{2u},Γ_2
Γ_7
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XBL 743-513

Fig. 2

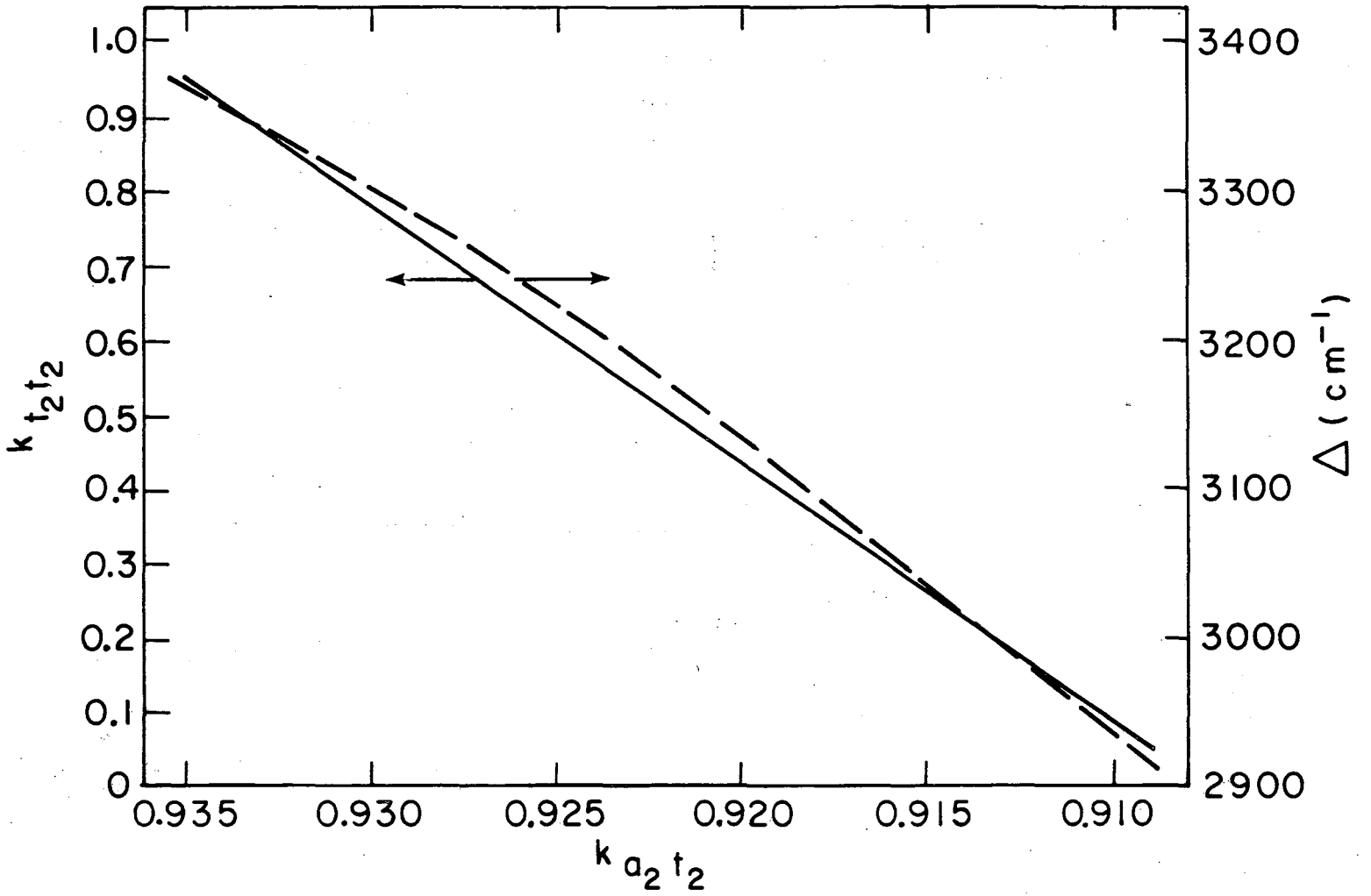

Fig. 3

XBL 769-3930

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