

when present, can occur in this gap and partly fill it so that such experiments could provide another check of the present theory.

Another case where fast-electron energy losses were observed is x-ray photoemission,¹⁸ where the electron created in the solid can excite both bulk and surface plasmons. The extension of our theory to this case could be worked out,¹⁵ though the situation here is more complicated by the presence of the hole. Its lifetime and the relaxation of the Fermi sea via low-energy electron-hole pair excitations modify the shape of the emitted-electron spectral lines.¹⁹ These effects could be treated in-

dependently of the discrete plasmon losses, but in thin films they might interfere with the surface plasmon emission from the region of strong dispersion.

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Analysis of the Magnetic Susceptibility of K_2OsCl_6

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The configuration interaction between the t_{2g}^4 and t_{2g}^3e configurations has been taken into account to calculate the energy levels of the $(OsCl_6)^{2-}$ complex ion in the intermediate-coupling scheme. The matrix elements of the magnetic moment operator between the ground level A_1 and the excited T_1 levels are given in algebraic form, and then used to calculate the temperature-independent paramagnetic susceptibility. The experimental value of the susceptibility and a part of the optical absorption spectrum can be fitted to theory by choosing the following values of the parameters: $B = 365.5 \text{ cm}^{-1}$, $C = 1561.0 \text{ cm}^{-1}$, $\xi_{5d} = 2575.0 \text{ cm}^{-1}$, $\Delta = 33\,000.0 \text{ cm}^{-1}$, $k = 0.7$, $k' = 0.7$.

I. INTRODUCTION

In complexes of the type X_2YZ_6 , where X is an

alkali ion [(or NH_4 , $C(NH_3)_4$, etc.)], Y is a metal ion of the 4d or 5d group, and Z is a halogen ion, unlike the corresponding complexes of the iron

group, the spin-orbit interaction is large and comparable in magnitude with the electrostatic interaction. Therefore, the spin-orbit interaction cannot be treated as a first-order perturbation to analyze the optical absorption spectra of the complexes. Further, the Kotani theory,¹ which assumed ζ_{nd} to be small and which was successful in the iron-group complexes, cannot be applied to explain their magnetic properties. The large value of the spin-orbit constant also makes it desirable to take into account the configuration interaction. A number of authors²⁻⁵ have done such complete calculations by simultaneously diagonalizing the crystal-field, electrostatic, and spin-orbit interactions for the octahedrally coordinated compounds where the central ion has two or three d electrons outside the closed shell. Schroeder⁶ has done intermediate-coupling calculations to interpret the optical spectrum of K_2IrCl_6 .

In this paper, we are interested in the analysis of the absorption spectrum and magnetic susceptibility of K_2OsCl_6 . According to Wyckoff,⁷ the structure of $(OsCl_6)^{2-}$ is such that the osmium ion ($5d^4$) is surrounded by six chlorine ions placed at the corners of an octahedron. We shall use this model for our purpose. Jørgensen⁸⁻¹⁰ has given the absorption spectrum of K_2OsCl_6 , and the experimental value of the magnetic susceptibility has also been reported.¹¹⁻¹⁴

II. CALCULATION OF ENERGY LEVELS

In a strong octahedral field, the d shell is split into a threefold subshell and a twofold subshell, labeled by the irreducible representations t_2 and e of the octahedral group. Strong-field states are constructed from the configuration $t_2^n e^m$ ($n \leq 6$, $m \leq 4$). The terms $S_1\Gamma_1$ of the t_2^n configuration, which are allowed by the exclusion principle, are coupled with the allowed terms $S_2\Gamma_2$ of e^m to give the resultant terms $S\Gamma$. The terms arising from the t_2^4 and t_2^3e configurations are as follows:

$$t_2^4: {}^3T_1, {}^1E, {}^1T_2, {}^1A_1$$

$$t_2^3e: {}^5E, {}^3A_1, {}^3A_2, {}^2^3E, {}^2^3T_1, {}^2^3T_2, {}^1A_1,$$

$${}^1A_2, {}^1E, {}^2^1T_1, {}^2^1T_2.$$

When the spin-orbit interaction is comparable with the electrostatic energy, the appropriate coupling scheme is $|t_2^n(S_1\Gamma_1)e^m(S_2\Gamma_2)S\Gamma t\rangle$. (This is analogous to the $|\alpha SLJ\rangle$ scheme in atomic spectroscopy). $S=0$ corresponds to the irreducible representation A_1 and $S=1$ corresponds to T_1 , etc. The spin S and space functions Γ are coupled to form bases for irreducible representations of the octahedral group. The spin-orbit interaction splits the $S\Gamma$ terms into t levels, e. g., 3T_1 is split into A_1 , E , T_1 , and T_2 (because $T_1 \times T_1 = A_1 + E + T_1 + T_2$). The spin-orbit interaction matrices, in this scheme,

are 6×6 , 8×8 , 11×11 , and 12×12 for A_1 , E , T_1 , and T_2 levels, respectively, which were taken from Schroeder.⁶ The A_2 levels, which come from the t_2^3e configuration, were ignored because they do not contribute to the magnetic susceptibility (see Sec. III). These matrices were combined with the corresponding matrices of electrostatic interaction, and the crystal-field parameter $\Delta (= 10Dq)$ was added in the diagonal interaction elements of the states arising from the t_2^3e configuration.

The absorption spectrum of K_2OsCl_6 has been measured by Jørgensen,⁸⁻¹⁰ and by far the best established level is the one at 17240 cm^{-1} , being the $t_2^4 {}^1A_1A_1$ level. The two broad bands at 10800 and 11700 cm^{-1} represent both E and T_2 components of $t_2^4 {}^1E$ and $t_2^4 {}^1T_2$. The combined interaction matrices were diagonalized on a fast computer for various values of the spin-orbit parameter ζ_{5d} , Racah parameters B and C , and the crystal-field

TABLE I. Calculated energy levels of K_2OsCl_6 .

Level	Energy (cm^{-1})	Dependence on			
		δB	δC	$\delta \zeta_{5d}$	$\delta \Delta$
A_1	0				
T_1	2 649.95	-0.0205	-0.3278	1.4326	-0.0157
T_2	4 461.99	0.4552	0.0886	1.8286	-0.0167
E	4 587.02	0.7985	-0.0212	1.9044	-0.0174
T_2	9 861.77	3.1688	1.3094	2.7753	-0.0147
E	10 110.79	4.7558	1.3801	2.6758	-0.0203
A_1	17 222.46	8.4160	4.0759	2.8224	0.0156
T_2	27 617.38	-5.0983	-5.0258	2.3456	0.9480
E	27 700.33	-5.0174	-4.9571	2.3804	0.9436
T_1	27 872.83	-4.9200	-4.9270	2.4893	0.9379
A_1	28 182.85	-5.0290	-5.0105	2.8042	0.9279
T_1	34 327.67	0.1210	-0.6971	1.5304	0.9524
T_1	35 412.42	-0.4186	-0.9455	2.1829	0.9521
A_1	35 432.87	-0.8167	-0.8529	2.4172	0.9345
T_2	35 833.56	0.0559	-1.1388	2.4038	0.9515
E	36 465.72	0.7775	-0.7644	2.5241	0.9356
T_1	36 861.06	0.3634	-1.0591	2.7256	0.9503
T_2	37 099.39	2.9305	-0.5956	2.1782	0.9499
E	37 387.73	0.2594	-1.0048	2.9991	0.9435
T_2	37 495.51	0.9279	-1.0446	2.9904	0.9419
T_1	37 667.45	3.2668	-1.2439	2.7681	0.9481
T_2	38 381.32	6.9480	-1.0636	2.3643	0.9519
T_1	39 234.36	8.1616	-1.2479	2.6486	0.9508
T_2	39 327.94	7.7159	-1.1623	2.8845	0.9362
T_2	40 808.66	5.8196	0.3449	2.6512	0.9489
T_1	42 112.25	6.4119	0.8885	2.7446	0.9489
E	42 289.43	10.8563	0.5371	2.3889	0.9494
E	45 015.70	16.9193	0.4934	2.6311	0.9481
T_2	45 128.93	15.1172	0.4284	3.0130	0.9446
T_2	45 420.63	12.6731	0.5407	3.3272	0.9510
T_1	45 897.27	17.4136	0.5234	2.8569	0.9503
A_1	46 268.35	23.3707	0.9358	2.6655	0.8910
T_1	46 801.60	14.8375	0.4998	3.5728	0.9515
E	47 222.29	14.9445	0.3086	4.0049	0.9384
A_1	48 218.81	16.5294	0.3304	4.0472	0.9467
T_1	50 053.70	19.3126	1.7476	3.4354	0.9522
T_2	51 756.96	24.2270	2.2762	3.2510	0.9387

TABLE II. Compositions of the levels of t_2^4 configuration and the first two T_1 levels of t_2^3e configuration.

Level	Energy (cm ⁻¹)	Composition
$t_2^3T_1A_1$	0	$0.94216t_2^3T_1 - 0.25484t_2^4A_1 - 0.13406t_2^3(A_2)e^5E$ $- 0.07375t_2^3(^2T_1)e^3T_1 + 0.12307t_2^3(^2T_2)e^3T_1$ $- 0.09402t_2^3(^2E)e^1A_1$
$t_2^3T_1T_1$	2649.95	$- 0.98404t_2^3T_1 - 0.12617t_2^3(A_2)e^5E - 0.05771t_2^3(^2E)e^3A_1$ $- 0.02807t_2^3(A_2)e^3E + 0.02705t_2^3(^2E)e^3E$ $+ 0.02590t_2^3(^2T_1)e^3T_1 - 0.06264t_2^3(^2T_2)e^3T_1$ $+ 0.02759t_2^3(^2T_1)e^3T_2 + 0.03879t_2^3(^2T_2)e^3T_2$ $- 0.05419t_2^3(^2T_1)e^1T_1 + 0.03299t_2^3(^2T_2)e^1T_1$
$t_2^3T_1T_2$	4461.99	$0.88849t_2^3T_1 - 0.42414t_2^4T_2 + 0.06782t_2^3(A_2)e^5E$ $- 0.03465t_2^3(^2E)e^3A_2 - 0.04056t_2^3(A_2)e^3E + 0.07619$ $t_2^3(^2E)e^3E + 0.09667t_2^3(^2T_1)e^3T_1 - 0.00565t_2^3(^2T_2)e^3T_1$ $- 0.00425t_2^3(^2T_1)e^3T_2 - 0.00767t_2^3(^2T_2)e^3T_2 - 0.01999$ $t_2^3(^2T_1)e^1T_2 - 0.08704t_2^3(^2T_2)e^1T_2$
$t_2^3T_1E$	4587.02	$- 0.90909t_2^3T_1 + 0.37894t_2^4E - 0.09787t_2^3(A_2)e^5E$ $- 0.06288t_2^3(^2T_1)e^3T_1 - 0.03874t_2^3(^2T_2)e^3T_1 - 0.09919$ $t_2^3(^2T_1)e^3T_2 - 0.06823t_2^3(^2T_2)e^3T_2 + 0.02058t_2^3(^2E)e^1E$
$t_2^4T_2T_2$	9861.77	$0.43435t_2^4T_1 + 0.88241t_2^4T_2 + 0.03788t_2^3(A_2)e^5E$ $+ 0.07713t_2^3(^2E)e^3A_2 - 0.03354t_2^3(A_2)e^3E - 0.05125$ $t_2^3(^2E)e^3E - 0.03954t_2^3(^2T_1)e^3T_1 + 0.04621t_2^3(^2T_2)e^3T_1$ $- 0.06182t_2^3(^2T_1)e^3T_2 - 0.07395t_2^3(^2T_2)e^3T_2 - 0.05047$ $t_2^3(^2T_1)e^1T_2 + 0.07756t_2^3(^2T_2)e^1T_2$
t_2^4EE	10110.79	$- 0.38357t_2^4T_1 - 0.90873t_2^4E - 0.04880t_2^3(A_2)e^5E$ $- 0.03784t_2^3(^2T_1)e^3T_1 + 0.05473t_2^3(^2T_2)e^3T_1 + 0.11753$ $t_2^3(^2T_1)e^3T_2 - 0.00940t_2^3(^2T_2)e^3T_2 + 0.07978t_2^3(^2E)e^1E$
$t_2^4A_1A_1$	17222.46	$0.28170t_2^4T_1 + 0.92603t_2^4A_1 - 0.05903t_2^3(A_2)e^5E$ $+ 0.00898t_2^3(^2T_1)e^3T_1 - 0.15229t_2^3(^2T_2)e^3T_1$ $+ 0.19064t_2^3(^2E)e^1A_1$
$t_2^3(A_2)e^5ET_1$	27872.83	$0.12139t_2^3T_1 - 0.96949t_2^3(A_2)e^5E + 0.05046$ $t_2^3(^2E)e^3A_1 + 0.00798t_2^3(A_2)e^3E - 0.03386t_2^3(^2E)e^3E$ $+ 0.04813t_2^3(^2T_1)e^3T_1 - 0.14228t_2^3(^2T_2)e^3T_1 - 0.06304$ $t_2^3(^2T_1)e^3T_2 - 0.11433t_2^3(^2T_2)e^3T_2 + 0.04087$ $t_2^3(^2T_1)e^1T_1 - 0.01767t_2^3(^2T_2)e^1T_1$
$t_2^3(A_2)e^3ET_1$	34327.67	$0.01452t_2^3T_1 + 0.01318t_2^3(A_2)e^5E + 0.20170$ $t_2^3(^2E)e^3A_1 + 0.56662t_2^3(A_2)e^3E + 0.33150t_2^3(^2E)e^3E$ $+ 0.45008t_2^3(^2T_1)e^3T_1 - 0.23747t_2^3(^2T_2)e^3T_1$ $+ 0.32478t_2^3(^2T_1)e^3T_2 + 0.31052t_2^3(^2T_2)e^3T_2 + 0.09292$ $t_2^3(^2T_1)e^1T_1 - 0.24183t_2^3(^2T_2)e^1T_1$

TABLE III. Matrix elements of $(L_z + 2S_z)$ between the A_1 and T_1 states.

T_1	$t_2^3(T_1)e^{-1}T_1$	$t_2^3(T_2)e^{-1}T_1$	$t_2^3(T_1)e^{-1}T_1$	$t_2^3(T_1)e^{-1}T_1$	$t_2^3(E)e^{-1}A_1$	$t_2^3(A_2)e^{-1}E$	$t_2^3(E)e^{-1}E$	$t_2^3(T_1)e^{-1}T_1$	$t_2^3(T_2)e^{-1}T_1$	$t_2^3(T_1)e^{-1}T_2$	$t_2^3(T_2)e^{-1}T_2$	$t_2^3(A_2)e^{-1}E$
$t_2^3(A_1)$	0	$4/\sqrt{3}ik'$	0	0	0	0	0	0	0	0	0	0
$t_2^3(E)e^{-1}A_1$	$-\sqrt{2}ik$	0	0	0	0	0	0	0	0	0	0	0
$t_2^3(T_1)$	0	0	$(2k+4)/\sqrt{6}i$	$2/3ik'$	$4/3ik'$	$2/3ik'$	0	$-1/\sqrt{3}ik'$	0	$1/\sqrt{3}ik'$	ik'	0
$t_2^3(T_1)e^{-1}T_1$	0	0	$-ik'$	$-2/\sqrt{6}ik$	0	$2/\sqrt{6}ik$	0	0	0	$1/\sqrt{2}ik$	0	0
$t_2^3(T_2)e^{-1}T_1$	0	0	$1/\sqrt{3}ik'$	0	0	0	0	$(4-k)/\sqrt{6}i$	0	0	$-1/\sqrt{2}ik$	0
$t_2^3(A_2)e^{-1}E$	0	0	0	0	0	0	0	0	0	0	0	$2/\sqrt{2}$

parameter Δ . The calculations were done in a self-consistent way in the sense that the energy levels were calculated to fit with the experimental spectrum and then the magnetic susceptibility (see Sec. III) was calculated with the same values of the parameters to see how close the agreement was. If the agreement between the calculated and experimental value of the susceptibility was not satisfactory, the parameters were changed slightly and the whole procedure was repeated. In this way, the following values of the parameters were obtained (all in units of cm^{-1}):

$$B = 365.5, \quad C = 1561.0, \tag{1}$$

$$\zeta_{5d} = 2575.0, \quad \Delta = 33\,000.0.$$

The calculated energy levels are given in Table I, which also gives approximate dependence of the energy levels on small changes in B , C , ζ_{5d} , and Δ from the above values. The levels arising from the t_2^3e configuration depend most heavily on the value of Δ , and also the dependence is nearly the same for all the levels. Therefore, a change in Δ will produce a nearly uniform shift in all these levels. Table I can also be used to calculate energy levels of other d^4 complexes of octahedral symmetry, such as $(\text{OsBr}_6)^{2-}$, etc. Table II gives the composition of the levels of the t_2^4 configuration and the first two T_1 levels of the t_2^3e configuration. The contributions of $t_2^4\ ^3T_1T_1$, $t_2^3(^4A_2)e^{-1}E$, and $t_2^2(^4A_2)e^{-1}E$ levels to the susceptibility are 95.0%, 0.4%, and 4.3%, respectively. All the other T_1 levels make a total contribution of 0.3%.

The low-lying levels belonging to the t_2^4 configuration are not very dependent on Δ . To reduce the number of parameters, we kept $\Delta = 33\,000\ \text{cm}^{-1}$ and made the assumption $C/B = 4.3$. In this approximation, the levels of the t_2^4 configuration are shown, in Fig. 1, as functions of ζ_{nd}/B .

III. SUSCEPTIBILITY

The temperature-independent paramagnetic susceptibility χ is given by¹⁵

$$\chi = \left(\frac{2}{3}N\beta^2\right) \sum_n |\langle \Psi_n | \vec{L} + 2\vec{S} | \Psi_0 \rangle|^2 / (E_n - E_0), \tag{2}$$

where N is Avogadro's number, β is the Bohr magneton, and the summation is over all the excited states. Both \vec{L} and \vec{S} transform as the irreducible representation T_1 . For the d^4 configuration, the lowest term is $t_2^4\ ^3T_1$ giving A_1 as the ground level, and, therefore, only those levels which transform as T_1 will have nonzero matrix elements with the ground level through the magnetic-moment operator (because $A_1 \times T_1 = T_1$). When the magnetic field is taken along the z axis and $E_n - E_0$ is expressed in units of cm^{-1} , Eq. (2) can be written as

$$\chi = 0.5106 \sum_n |\langle \Psi_n | (L_z + 2S_z) | \Psi_0 \rangle|^2 / (E_n - E_0). \tag{3}$$

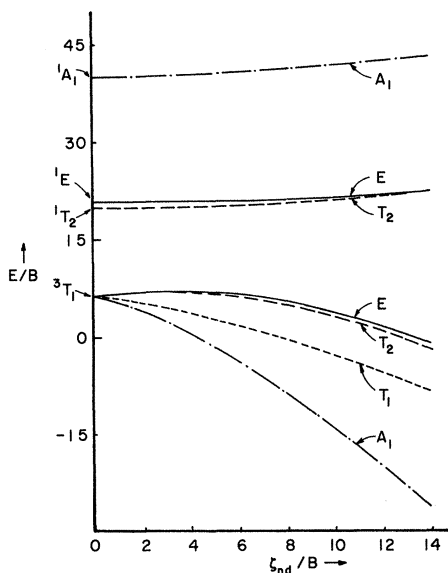


FIG. 1. Energy-level diagram for the t_2^4 configuration.

We also note that \vec{L} is a one-electron operator and therefore it can connect only those levels which belong to the configurations which differ at the most in one electron (e. g., levels belonging to t_2^n and $t_2^{n-1}e$ but not t_2^n and $t_2^{n-2}e^2$). Further, \vec{S} is also a one-electron operator, but it can have interaction only within a configuration because of the orthogonality of spatial functions belonging to different configurations.

The compositions of Ψ_0 and Ψ_n are already known from the analysis of the absorption spectrum. If we calculate the matrix elements of the magnetic-moment operator between the ground level A_1 and the excited levels T_1 , we can calculate the susceptibility from Eq. (3). Tensor-operator methods¹⁶ were used to calculate the matrix elements of the magnetic-moment operator, and they are given in Table III. The matrix elements of L_x are multiplied by the orbital reduction factors k and k' , defined in terms of the one-electron orbital-angular-momentum operator \vec{l} as

$$\langle t_2 \| \vec{l} \| t_2 \rangle = \sqrt{6}ik,$$

$$\langle t_2 \| \vec{l} \| e \rangle = -2\sqrt{3}ik'.$$

k and k' are generally less than unity, and k is not

TABLE IV. Calculated susceptibility for a few values of the orbital reduction factors.

k	k'	$10^6\chi$
1.0	1.0	1190
0.8	0.8	1007
0.8	0.7	987
0.7	0.8	942
0.7	0.7	922
0.6	0.6	842

necessarily equal to k' but $k=k'=1$ for the pure d orbitals. $1-k$ and $1-k'$ may, therefore, be regarded as a measure of the departure of the actual orbitals from being pure d orbitals.

Since the orbital reduction factor k' appears multiplied with the matrix elements of L_x between states belonging to the t_2^4 and t_2^3e configuration, for which $(E_n - E_0)$ in Eq. (3) is very large (see Table I), the calculated susceptibility is not as sensitive to changes in k' as to changes in k . The susceptibility was calculated, with parameters of Eq. (1), for a few values of the orbital reduction factors, and the results are given in Table IV. If we take $k=0.7$ and $k'=0.7$, the value of susceptibility is 922×10^{-6} . Unfortunately, the experimental values of susceptibility in literature vary from 860×10^{-6} to 941×10^{-6} , and the average value is $908 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ (see Ref. 12 for details).

Griffith¹⁵ gave the following analytical expression for the susceptibility of t_2^4 :

$$\chi = 2N\beta^2(k+2)^2(1+\cos\theta)/3m\delta, \quad (4)$$

where $m = \frac{1}{2}\xi_{nd} + \delta(\sec\theta - 1)$, $2\delta = 15B + 5C + \xi_{nd}$, and $\delta \tan\theta = \sqrt{2}\xi_{nd}$. According to the present calculations the susceptibility from the states belonging to the t_2^4 configuration is 895×10^{-6} and the rest comes from the high-frequency elements. This may be compared with 1136×10^{-6} , given by Eq. (4). The reason for this difference is that in the above formula for χ , T_1 is taken as pure $t_2^3T_1T_1$, and A_1 is a combination of $t_2^3T_1A_1$ and $t_2^4A_1$. However, when the states of the t_2^3e configuration are included, both A_1 and T_1 are diluted by them, and the value of χ becomes less than that given by Eq. (4). Also, the value of m , which is the energy difference between $t_2^3T_1T_1$ and $t_2^3T_1A_1$, is 2084 cm^{-1} compared with 2650 cm^{-1} calculated in this work, and this reduces the value of χ given by Eq. (4).

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