

Transition Probabilities for the Excited State $d\epsilon^3 {}^2\Gamma_3$ of Cr^{3+}

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In recent experiments Geschwind has observed transitions between the Zeeman components of the excited metastable state $d\epsilon^3 {}^2\Gamma_3$ of trivalent chromium present as a dilute impurity in Al_2O_3 . In first order the transitions are forbidden. In third order a number of processes give rise to a transition probability and predict $g_1=0.1$, consistent with the experimental observations. The magnetic moment associated with the transition is shown to rotate opposite to the usual sense.

IN a recent letter¹ Geschwind, Collins, and Schawlow describe the detection of microwave transitions between the Zeeman components of the metastable excited state $d\epsilon^3 {}^2\Gamma_3$ of Cr^{3+} , present as a dilute impurity in Al_2O_3 . The state ${}^2\Gamma_3$ is two-fold spin degenerate and two-fold orbitally degenerate, and we may designate the four components as ${}^2\Gamma_3(1, \frac{1}{2})$, ${}^2\Gamma_3(1, -\frac{1}{2})$, ${}^2\Gamma_3(-1, \frac{1}{2})$, and ${}^2\Gamma_3(-1, -\frac{1}{2})$, where $\pm\frac{1}{2}$ is the spin quantum number and ± 1 is an orbital quantum number describing the transformation properties of the wave functions under rotation around the axis of quantization which is taken to be the trigonal axis of the crystal. Under the combined action of spin-orbit coupling and the trigonal crystal field the state ${}^2\Gamma_3$ splits into two Kramer's doublets separated by about 30 cm^{-1} . The upper doublet is comprised of the states ${}^2\Gamma_3(1, \frac{1}{2})$ and ${}^2\Gamma_3(-1, -\frac{1}{2})$, while the lower doublet contains the states ${}^2\Gamma_3(1, -\frac{1}{2})$ and ${}^2\Gamma_3(-1, \frac{1}{2})$. In an applied magnetic field, these latter states split and give rise to the microwave transitions observed by Geschwind, Collins, and Schawlow.¹ Since no matrix components of angular momentum \mathbf{L} exist in Γ_3 , and since the spin \mathbf{S} cannot affect the orbital quantum number, it is clear that

$$[{}^2\Gamma_3(1, -\frac{1}{2}) | \mathbf{L} + 2\mathbf{S} | {}^2\Gamma_3(-1, \frac{1}{2})]$$

vanishes, and that the transitions are forbidden to first order. It is of interest therefore to identify the processes that give rise to a nonzero transition probability.

The energy levels of the Cr^{3+} system of importance in the following discussion are shown in Fig. 1 which is similar to a diagram given by Sugano and Tanabe,² and includes some additional levels. The levels are designated in the strong field representation, and the existing matrix components are indicated by arrows. The approximate experimental position for each level above the ground state $d\epsilon^3 {}^4\Gamma_2$ is shown in wave numbers. The numbers in brackets are calculated from the value of the parameter B discussed below. V_{so} is the spin-orbit interaction, V_t the trigonal crystal field, V_c the Coulomb interaction, and \mathbf{L} the orbital angular momentum.

A variety of processes give rise to a matrix component of $(\mathbf{L}+2\mathbf{S})$ in the third order. The most important of

these involve the close-lying level $d\epsilon^3 {}^2\Gamma_4$ and are tabulated below:

$$\begin{aligned} & [{}^2\Gamma_3(1, -\frac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_4(0, -\frac{1}{2}) | V_{so} | {}^2\Gamma_5(-1, \frac{1}{2})] \\ & \times [{}^2\Gamma_5(-1, \frac{1}{2}) | V_t | {}^2\Gamma_3(-1, \frac{1}{2})] = 2\zeta K k, \quad (1) \end{aligned}$$

$$\begin{aligned} & [{}^2\Gamma_3(1, -\frac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_4(0, -\frac{1}{2}) | V_{so} | {}^2\Gamma_5(-1, \frac{1}{2})] \\ & \times [{}^2\Gamma_5(-1, \frac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \frac{1}{2})] = -\frac{1}{3}\zeta^2 k, \quad (2) \end{aligned}$$

$$\begin{aligned} & [{}^2\Gamma_3(1, -\frac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_4(0, -\frac{1}{2}) | V_{so} | {}^2\Gamma_5(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_5(0, -\frac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \frac{1}{2})] = -\frac{2}{3}\zeta^2 k, \quad (3) \end{aligned}$$

$$\begin{aligned} & [{}^2\Gamma_3(1, -\frac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_4(0, -\frac{1}{2}) | V_c | {}^2\Gamma_4'(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_4'(0, -\frac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \frac{1}{2})] = 6\zeta B k, \quad (4) \end{aligned}$$

$$\begin{aligned} & [{}^2\Gamma_3(1, -\frac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\frac{1}{2})] \\ & \times [{}^2\Gamma_4(0, -\frac{1}{2}) | V_{so} | {}^2\Gamma_3'(-1, \frac{1}{2})] \\ & \times [{}^2\Gamma_3'(-1, \frac{1}{2}) | V_c | {}^2\Gamma_3(-1, \frac{1}{2})] = 6\zeta B k, \quad (5) \end{aligned}$$

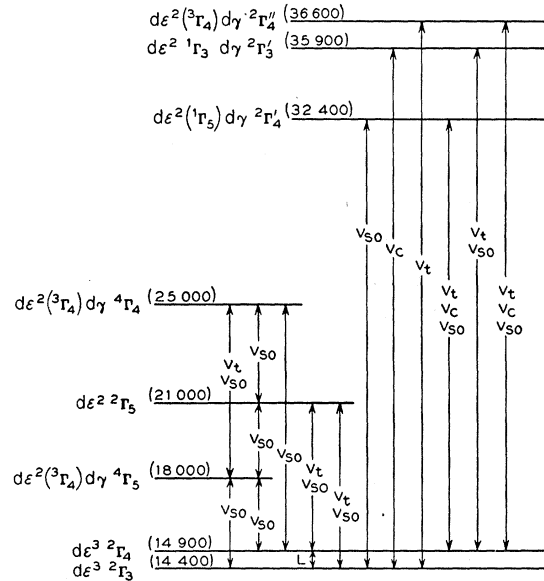


FIG. 1. Excited energy levels of Cr^{3+} in a cubic crystal field.

¹ S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters **3**, 545 (1959).

² S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

TABLE I. Contributions to g_1 from processes 1 to 10.

Process	Contribution
1	$-0.0297k$
2	$-0.0020k$
3	$-0.0040k$
4	$+0.0655k$
5	$+0.0547k$
6	$-0.0048k$
7	$-0.0024k$
8	$+0.0011k$
9	$-0.0044k$
10	$+0.0109k$
Total	$0.0849k$

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_4(0, -\tfrac{1}{2}) | V_{so} | {}^4\Gamma_5(0, -\tfrac{1}{2})] \\
& \times [{}^4\Gamma_5(0, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \tfrac{1}{2})] = -(4/9)\zeta^2 k, \quad (6)
\end{aligned}$$

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_4(0, -\tfrac{1}{2}) | V_{so} | {}^4\Gamma_5(-1, \tfrac{1}{2})] \\
& \times [{}^4\Gamma_5(-1, \tfrac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \tfrac{1}{2})] = -(2/9)\zeta^2 k, \quad (7)
\end{aligned}$$

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_4(0, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_4'(-1, \tfrac{1}{2})] \\
& \times [{}^2\Gamma_4'(-1, \tfrac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \tfrac{1}{2})] = \tfrac{1}{2}\zeta^2 k, \quad (8)
\end{aligned}$$

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_4(0, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_4''(-1, \tfrac{1}{2})] \\
& \times [{}^2\Gamma_4''(-1, \tfrac{1}{2}) | V_t | {}^2\Gamma_3(-1, \tfrac{1}{2})] = +\zeta K k, \quad (9)
\end{aligned}$$

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | L_+ | {}^2\Gamma_4(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_4(0, -\tfrac{1}{2}) | V_t | {}^2\Gamma_4'(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_4'(0, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \tfrac{1}{2})] = -2\zeta K k. \quad (10)
\end{aligned}$$

These matrix elements are obtained from the tables prepared by Tanabe and Sugano³ and Tanabe and Kamimura.⁴ Each process is supplemented by another, of equal magnitude, in which $L_+ = (L_x + iL_y)$ appears at the opposite end of the chain. In these expressions, ζ is the effective spin-orbit coupling parameter for the d electrons and has been found by Sugano and Tanabe² to equal 140 cm^{-1} from the splitting of ${}^2\Gamma_3$. The quantity K measures the strength of the trigonal field and has been estimated by Sugano and Tanabe² to equal -350 cm^{-1} from the splittings of ${}^4\Gamma_5$ and ${}^4\Gamma_4$. The parameter k measures the reduction of the orbital angular-momentum matrix components in the $d\epsilon$ wave functions, and has been estimated by Sugano and Tanabe² to be equal to 0.6. B is the usual Racah parameter and determines the Coulomb interaction between the levels ${}^2\Gamma_4$, ${}^2\Gamma_4'$ and ${}^2\Gamma_3$, ${}^2\Gamma_3'$. It may be estimated by fitting the position of the levels ${}^4\Gamma_5$ and ${}^4\Gamma_4$,³ and an appropriate value for the present case is 700 cm^{-1} . The corresponding matrix elements of $L_- = (L_x - iL_y)$ are all zero.

³ Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954).

⁴ Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan **13**, 394 (1958).

The interaction of the microwave field \mathbf{h} with the ion may be written $\mu_B \mathbf{h} \cdot (\mathbf{L} + 2\mathbf{S})$ where μ_B is the Bohr magneton. We set the matrix element of this interaction equal to $\frac{1}{2} g_1 \mu_B h_-$ where g_1 is the matrix element of L_+ between the components of the doublet, and $h_- = h_x - ih_y$. If the transition were between the components of an ordinary spin doublet, g_1 would be 2. The contributions to g_1 listed in Eqs. (1-10) are found by dividing by the appropriate energy denominators in each case and are listed in Table I. The processes omitted from this table give much smaller contributions to g_1 . For example, the two cases

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | V_{so} | {}^4\Gamma_5(0, \tfrac{1}{2})] \\
& \times [{}^4\Gamma_5(0, \tfrac{1}{2}) | 2S_+ | {}^4\Gamma_5(0, -\tfrac{1}{2})] \\
& \times [{}^4\Gamma_5(0, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \tfrac{1}{2})] = -(4/9)\zeta^2, \quad (11)
\end{aligned}$$

$$\begin{aligned}
& [{}^2\Gamma_3(1, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_5(1, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_5(1, -\tfrac{1}{2}) | L_+ | {}^2\Gamma_5(0, -\tfrac{1}{2})] \\
& \times [{}^2\Gamma_5(0, -\tfrac{1}{2}) | V_{so} | {}^2\Gamma_3(-1, \tfrac{1}{2})] = \tfrac{1}{3}\zeta^2 k, \quad (12)
\end{aligned}$$

give contributions of -0.00068 and $0.00015k$, respectively. The final total listed in Table I must be doubled for the reason discussed above. Consequently the theoretical value of g_1 is $0.170k$. If we adopt the value $k=0.6$ estimated by Sugano and Tanabe,² $g_1 = 0.102$. It will be noticed that the largest contribution to g_1 arises from the configuration interaction between levels of type $d\epsilon^3$ and $d\epsilon^2 d\gamma$.

Geschwind, Collins, and Schawlow have determined g_1 directly from the angular dependence of the field for resonance to be less than 0.06.¹ A more recent analysis of the limits of error, including the effects of crystal twinning,⁵ places g_1 less than 0.2. The theoretical value is therefore consistent with the experimental observation.

We have determined above that a transition is made from the state ${}^2\Gamma_3(-1, \tfrac{1}{2})$ to the state ${}^2\Gamma_3(1, -\tfrac{1}{2})$ by way of the interaction $\frac{1}{2}\mu_B h_- L_+$. If the states formed an ordinary spin doublet, the transition would be caused by the interaction $\mu_B h_+ S_-$. Consequently the sense of rotation of the transition is opposite to that of a transition between the states of a normal spin doublet. In accordance with a recent discussion by Pryce,⁶ the parallel g value in the spin Hamiltonian for the excited state must be taken to be negative. The reversed sense of rotation has interesting implications concerning the relaxation of the excited doublet by way of cross relaxation with ground-state transitions.

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⁵ S. Geschwind (private communication).

⁶ M. H. L. Pryce, Phys. Rev. Letters **3**, 375 (1959).