

where the $\int_{\epsilon} dS_k$ is taken over the surface of constant energy ϵ in \vec{k}' space and is of order $n(\epsilon)A_s J_{sd}$. We denote this integral $U(\vec{k}', \vec{k}, \epsilon)$ and assume it to be a well-behaved function of ϵ for \vec{k} and \vec{k}' values of interest. In performing $\int d\epsilon$ in (A2), it is shown by Schiff²¹ that the path of integration should pass under singularities on the real axis. The final result for the first term in (A1) then becomes

$$\frac{1}{4}m_s \langle m+1 | I^+ | m \rangle \left\{ \int_{\mathcal{P}} \frac{U(\vec{k}', \vec{k}, \epsilon) d\epsilon}{(\epsilon_{\vec{k}} - \epsilon)} \right.$$

$$\left. + i\pi U(\vec{k}', \vec{k}, \epsilon_{\vec{k}}) \right\}. \quad (A3)$$

Barring irregular behavior of U , the quantity in large parentheses in (A3) is of order $A_s J_{sd} / \epsilon_F$ as was to be shown.

The above argument can be carried through in a similar fashion for process (b) of Table I as well, leading to the conclusion that terms (a) and (b) both produce relatively small corrections to the Korringa process.

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Further EPR Studies of Forbidden Hyperfine Transitions of Mn^{2+} in Calcite*

V. Lupei† and A. Lupei†

Argonne National Laboratory, Argonne, Illinois 60439

and

I. Ursu

Institute for Atomic Physics, Bucharest, Romania

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A study of the forbidden hyperfine transitions up to $\Delta m = \pm 5$ within the central fine-structure component of the EPR spectrum of Mn^{2+} in calcite is reported. The line positions are interpreted with spin-Hamiltonian parameters previously determined and with a quadrupole-interaction parameter of 0.5 ± 0.1 G. Two approaches were used for calculating line intensities; perturbation theory and the effective-electron-magnetic field method. Good agreement with experiment was obtained.

INTRODUCTION

Forbidden hyperfine transitions ($\Delta M = \pm 1$, $\Delta m \neq 0$) have been observed in the electron-paramagnetic-resonance (EPR) spectra of Mn^{2+} in a series of crystals. The great majority of these investiga-

tions have dealt with $\Delta M = \pm 1$, $\Delta m = \pm 1$ transitions, while transitions of larger values of Δm have seldom been considered. Important requirements for the occurrence of forbidden transitions in the spectrum of the Mn^{2+} (⁶S) ion are that (i) the fine-structure parameter be large enough, and (ii) the lines

be narrow and well resolved. In the case of calcite, the not very large fine-structure parameter is somewhat compensated by the extreme narrowness of the lines, resulting in a great variety of forbidden transitions.

Although there is evidence for $\Delta M = \pm 1$, $\Delta m = \pm 1$ forbidden transitions in the EPR spectra of Mn^{2+} in calcite observed by Hurd, Sachs, and Herschberger,¹ the first one to note their existence was Mataresse.² Subsequently, the forbidden transitions $\Delta M = \pm 1$, $\Delta m = \pm 1$, and ± 2 were studied by us^{3,4} using the third-order perturbation theory; we also reported the appearance in the spectra of the transitions with $\Delta M = \pm 1$, $\Delta m = \pm 3$. Transitions of $\Delta M = \pm 1$, $\Delta m = \pm 1$, and ± 2 were reported by Lazukin and co-workers.^{5,6} Transitions of $\Delta M = \pm 1$, $\Delta m = \pm 1$ were examined with the help of the second-order perturbation theory and by diagonalization of the full matrix by Mankowitz and Low.⁷

We have been able to observe the hyperfine transitions with $\Delta M = \pm 1$, $\Delta m = \pm 4$, and ± 5 .⁸ In this paper we deal mainly with the transition probabilities and with some facts concerning the line positions which have not been reported previously.

EXPERIMENT

The samples were natural calcite single crystals with Mn^{2+} ion present as a substitutional impurity (0.001–0.01 at. %). In the calcite lattice, Mn^{2+} is surrounded by an octahedron of oxygens, distorted along one of the $\langle 111 \rangle$ axes, parallel to the macroscopic c axis of the crystal. There are two magnetic complexes in the unit cell related to each other by a rotation about the c axis of the crystal.

The EPR measurements were carried out at room, liquid-nitrogen, and liquid-helium temperatures, in the X , K , and Q microwave bands. The observed spectra are very complex and show a strong angular dependence. The forbidden transitions were studied in the central lines, since their probability is maximum in this region. We have

used calcite crystals with a pronounced mosaicity. This leads to a strong broadening of the outer and intermediate fine-structure lines, but affects to a much lesser extent the central fine-structure component. In this situation the superposition of the lines of the various fine-structure sets does not interfere with the study. However, this mosaic structure unequally affects the width of the six hyperfine components of the central fine-structure transition. Consequently, in the study of the line intensities we have taken the quantity $(\Delta H)^2/h$ as a measure of the area under the absorption curve, ΔH being the linewidth between the extrema of the first derivative curve and h its height. We note that the shape of all the hyperfine-structure components was practically the same.

The positions of the forbidden transitions depend on the orientation of the sample in the external magnetic field. For a limited range of the polar and azimuthal angles θ and φ , we observed an additional splitting of the forbidden transitions. This splitting was observed only in the X band at low temperatures (liquid-nitrogen and liquid-helium temperatures) and is clearly seen in Fig. 2 of Ref. 3 for the $\Delta M = \pm 1$, $\Delta m = \pm 1$, and ± 2 transitions. This splitting is consistent with the existence of two inequivalent cation positions in the lattice. It must be noticed that the transitions $\Delta m = k$ and $\Delta m = -k$ are unequally split for the same value of m .

Because of the very strong dependence of the line intensities on $k = |\Delta m|$ and on the orientation, it was very difficult to follow the forbidden lines with $k > 2$ in the whole range of orientations. However, the agreement between the observed and calculated line positions and intensities is fairly good within the observation range.

THEORY

The point symmetry of the Mn^{2+} site in the calcite lattice is 6S hence the spin Hamiltonian used for the interpretation of the spectra is⁹

$$\begin{aligned} \mathcal{H} = & g\mu_B H S_x + K S_x I_x + \frac{1}{4} \left(\frac{AB}{K} - B \right) (S_+ I_+ + S_- I_-) + \frac{1}{4} \left(\frac{AB}{K} + B \right) (S_- I_+ + S_+ I_-) + \frac{B^2 - A^2}{4K} (S_+ + S_-) I_x \sin 2\beta \\ & + \frac{1}{2} Q \left(3 \frac{A^2}{K^2} \cos^2 \beta - 1 \right) (I_x^2 - \frac{1}{3} I(I+1)) - \frac{1}{2} \frac{AB}{K^2} Q \sin 2\beta [(I_x - \frac{1}{2}) I_+ + (I_x + \frac{1}{2}) I_-] \\ & + \frac{1}{4} Q \frac{B^2}{K^2} \sin^2 \beta (I_+^2 + I_-^2) - \gamma \mu_N \frac{A g_{\parallel} \cos^2 \theta + B g_{\perp} \sin^2 \theta}{K g} H I_x - \gamma \mu_N \frac{A g_{\parallel} - B g_{\perp}}{4 K g} H \sin 2\theta (I_+ + I_-) \\ & + \frac{1}{6} D (3 \cos^2 \beta - 1) O_2^0 - D \sin 2\beta O_2^1 + \frac{1}{2} D \sin^2 \beta O_2^2 - \frac{\alpha - F}{180} \{ \frac{1}{6} (35 \cos^4 \beta - 30 \cos^2 \beta + 3) O_4^0 \\ & + \frac{5}{2} \sin 2\beta (3 - 7 \cos^2 \beta) O_4^1 - \frac{5}{2} (7 \cos^4 \beta - 8 \cos^2 \beta + 1) O_4^2 - 35 \cos \beta \sin^3 \beta O_4^3 + \frac{35}{8} \sin^4 \beta O_4^4 \} \\ & + \frac{\alpha \sqrt{2}}{9} \cos 3\varphi \left(\frac{1}{8} \sin^3 \beta \cos \beta O_4^1 - \frac{1}{4} (4 \cos^4 \beta - 5 \cos^2 \beta + 1) O_4^1 \right) \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \sin \beta \cos^3 \beta O_4^2 + \frac{1}{4} (4 \cos^4 \beta + 3 \cos^2 \beta - 3) O_4^3 - \frac{1}{16} \sin 2\beta (\cos^2 \beta + 3) O_4^4 - \frac{a\sqrt{2}}{9} \\
& \times \sin 3\varphi \left(\frac{3}{4} \cos \beta \sin^2 \beta O_4^{1*} + \frac{1}{4} \sin \beta (3 \cos^2 \beta - 1) O_4^{2*} + \frac{1}{4} \cos \beta (9 \cos^2 \beta - 5) O_4^{3*} - \frac{1}{8} \sin \beta (3 \cos^2 \beta + 1) O_4^{4*} \right),
\end{aligned} \tag{1}$$

where

$$\cos \beta = (g_{\parallel}/g) \cos \theta, \quad \sin \beta = (g_{\perp}/g) \sin \theta.$$

The derivation of this spin Hamiltonian is given in the Appendix.

The energy levels were computed by perturbation theory up to the third order. By using the selection rules for the various transitions, the

corresponding resonance fields and the forbidden-doublet splittings were calculated. The forbidden doublet is defined as the difference between the resonance fields for the transitions with $\Delta m = +k$ and $-k$. After labeling the forbidden transitions with $|M-1, \lambda - \frac{1}{2}k\rangle \leftrightarrow |M, \lambda + \frac{1}{2}k\rangle$ and $|M-1, \lambda + \frac{1}{2}k\rangle \leftrightarrow |M, \lambda - \frac{1}{2}k\rangle$, where $\lambda = m - \frac{1}{2}$ for odd k and $\lambda = m$ for even k , the expression for the forbidden-doublet separation $\Delta H_k(\lambda)$ is

$$\begin{aligned}
\Delta H_k(\lambda) = & H_{|M-1, \lambda - k/2\rangle \rightarrow |M, \lambda + k/2\rangle} - H_{|M-1, \lambda + k/2\rangle \rightarrow |M, \lambda - k/2\rangle} = k \left[\frac{17}{2} \frac{AB^2}{K} \frac{1}{H} - \frac{67}{2} \frac{AB^2}{H^2} \lambda \right. \\
& + 2 \frac{\gamma \mu_N}{\mu_B} H \frac{Ag_{\parallel} \cos^2 \theta + Bg_{\perp} \sin^2 \theta}{Kg^2} - 2Q \left(3 \frac{A^2}{K^2} \cos^2 \beta - 1 \right) \lambda - 4D \frac{B^2 - A^2}{K} \frac{1}{H} \sin^2 2\beta \\
& + \frac{17}{4} \frac{B^2}{K^2} (A^2 + K^2) \frac{Ag_{\parallel} \cos^2 \theta + Bg_{\perp} \sin^2 \theta}{Kg^2} \frac{\gamma \mu_N}{\mu_B} \frac{1}{H} + 4 \frac{A^2 + K^2}{K^2} \frac{B^2 D}{H^2} (3 \cos^2 \beta - 1) \lambda \\
& \left. + \frac{5}{6} (A^2 + K^2) \frac{B^2}{K^2} \frac{a-F}{H^2} (35 \cos^4 \beta - 30 \cos^2 \beta + 3) \lambda - \frac{50\sqrt{2}}{3} (A^2 + K^2) \frac{B^2}{K^2} \frac{a}{H^2} \sin^3 \beta \cos \beta \cos 3\varphi \right].
\end{aligned} \tag{2}$$

The last term in Eq. (2) predicts an azimuthal dependence of the forbidden doublet, in agreement with the experiment. This term arises from a different φ dependence of the two forbidden lines of the doublet. The fact that the φ angle for the two magnetic complexes differs by the angle α leads to a splitting of the forbidden and allowed hyperfine components of the central fine-structure component due to the terms of the type

$$\frac{(A^2 + K^2) B^2}{K^2} \frac{a}{H^2} \sin^3 \beta \cos \beta \cos 3\varphi.$$

Clearly, for a given orientation of the crystals the forbidden-doublet splitting will also be different for the two complexes.

As previously pointed out, the quadrupole-inter-

action parameter enters as a first-order term in the expression of the forbidden-doublet splitting. Consequently, the study of the forbidden hyperfine transitions should lead to such a parameter. The determination of Q with the help of Eq. (2) must be performed taking into account the significant terms of order H^{-2} . To avoid the complications caused by the presence of the two inequivalent positions, it is recommendable to perform the θ -dependence measurements of the forbidden doublet in a φ plane for which the last term in Eq. (2) vanishes.

The most convenient method to measure the Q parameter using the forbidden hyperfine transitions is to make the difference between the two outer forbidden-doublet splittings of the same order:

$$\Delta = \Delta H_k(\lambda_{\max}) - \Delta H_k(\lambda_{\min}) = \left[\frac{67}{2} \frac{AB^2}{H^2} - 2Q \left(3 \frac{A^2}{K^2} \cos^2 \beta - 1 \right) + 4 \frac{A^2 + K^2}{K^2} B^2 \frac{D}{H^2} (3 \cos^2 \beta - 1) \right] k (\lambda_{\max} - \lambda_{\min}). \tag{3}$$

This difference has the maximum value, when $k(\lambda_{\max} - \lambda_{\min})$ reaches its maximum allowed value, i. e., for the transition with $k=2$ and 3, when $k(\lambda_{\max} - \lambda_{\min})=6$. Because the $k=3$ forbidden hyperfine transitions are very weak, the most suitable forbidden transitions for the evaluation of the quad-

rupole interaction parameter are those corresponding to $k=2$. With this method we have estimated $Q = 0.5 \pm 0.1$ G for Mn^{2+} in calcite. We were not able to observe the 2φ dependence of the forbidden hyperfine transitions, predicted by the term $Q'' [I_x^2 + I_y^2]$ in the spin Hamiltonian of Eq. (3),

Ref. 7.

The transition probabilities for the allowed and forbidden hyperfine transitions were computed with the perturbation method and with the more accurate

method of the effective electron magnetic field.

The expressions for the transition probabilities, obtained by using the eigenfunctions computed with the perturbation method, are

$$P|\frac{1}{2}, m\rangle \leftrightarrow |-\frac{1}{2}, m\rangle \propto 9 \left[1 - 128 \frac{A^2 B^2}{K^2} R^2 \frac{1}{H^2} \left(\frac{35}{4} - m^2 \right) - 4 \frac{D^2}{H^2} \sin^2 2\beta - B^2 \frac{K^2 + A^2}{K^2} \frac{1}{H^2} \left(\frac{35}{4} - m^2 \right) - \frac{D^2}{H^2} \sin^4 \beta + \frac{4}{3} \frac{D^2}{H^2} \sin 2\beta (3 \cos^2 \beta - 1) \right], \quad (4)$$

$$P|-\frac{1}{2}, m\rangle \leftrightarrow |\frac{1}{2}, m-1\rangle \propto 576 \frac{A^2 B^2}{K^4} R^2 \frac{1}{H^2} \left(\frac{35}{4} - m^2 + m \right) \left(1 - 64 \frac{A^2 B^2}{K^4} \frac{R^2}{H^2} \right), \quad (5)$$

$$P|-\frac{1}{2}, m-1\rangle \leftrightarrow |\frac{1}{2}, m+1\rangle \propto 2304 \left(\frac{AB}{K^2} \right)^4 \frac{R^4}{H^4} \left(\frac{35}{4} - m^2 - m \right) \left(\frac{35}{4} - m^2 + m \right), \quad (6)$$

where

$$R = D \sin 2\beta - \frac{5}{24} (a - F) \sin 2\beta (3 - 7 \cos^2 \beta) - \frac{5}{12} \sqrt{2} a (4 \cos^4 \beta - 5 \cos^2 \beta - 1) \cos 3\varphi.$$

It must be noted that Eqs. (4)–(6) are valid only for small values of the fine-structure parameter D (under 100 G). For larger values of this parameter, higher-order terms must be taken into account in the expression for the transition probabilities.

In the method of the effective electron magnetic field, it is assumed that the quantization axis for the nuclear spin is determined by the accurate effective magnetic field at the nucleus created by the electrons. The interaction is thus regarded as being equivalent to a Zeeman-type interaction. The calculation of the effective magnetic field is accomplished by averaging the hyperfine interaction over the electron wave functions, which are the eigenstates of the electronic Zeeman and fine-structure terms in the spin Hamiltonian.^{10,11} This effective field depends on the quantum number M . As a consequence, the eigenfunctions of the nuclear spin in this effective magnetic field will depend on M . The eigenfunctions of the system may be written as products of the pure "electronic" eigenfunctions $|M\rangle$ and the nuclear eigenfunctions $|m(M)\rangle$:

$$|Mm\rangle = |M\rangle |m(M)\rangle. \quad (7)$$

The nuclear eigenfunctions $|m(M)\rangle$, determined by an effective field H_{eff}^M corresponding to the $|M\rangle$ electronic state, can be expressed as linear combinations of functions determined by another field $H_{\text{eff}}^{M'}$, corresponding to the $|M'\rangle$ electronic state,

according to the relation

$$|m(M)\rangle = \sum_{m'} d_{mm'}^{(I)}(\omega) |m'(M')\rangle, \quad (8)$$

where $d_{mm'}^{(I)}(\omega)$ are matrix elements of the irreducible representation of the rotation group, and ω is the rotation which carries the direction H_{eff}^M over into $H_{\text{eff}}^{M'}$. We will express this rotation by $\mu = \cos(H_{\text{eff}}^M, H_{\text{eff}}^{M'})$ in the plane determined by the two magnetic fields.

A microwave magnetic field perpendicular to the external magnetic field will induce transitions between the states $|m(M)\rangle$ and the probability is proportional to

$$\begin{aligned} & |\langle Mm(M) | S_+ + S_- | M'm'(M') \rangle|^2 \\ &= |\langle M | S_+ + S_- | M' \rangle|^2 |\langle m(M) | m'(M') \rangle|^2 \\ &= |\langle M | S_+ + S_- | M' \rangle|^2 |d_{mm'}^{(I)}(\mu)|^2. \end{aligned} \quad (9)$$

For the central fine-structure component the first factor in this product is, in the H^{-2} approximation,

$$\begin{aligned} & |\langle \frac{1}{2} | S_+ + S_- | -\frac{1}{2} \rangle|^2 = 9 \left(1 - 4 \frac{D^2}{H^2} \sin^2 2\beta - \frac{D^2}{H^2} \sin^4 \beta \right. \\ & \quad \left. + \frac{4}{3} \frac{D^2}{H^2} (3 \cos^2 \beta - 1) \sin 2\beta \right), \end{aligned} \quad (10)$$

where we neglected the contribution of the fourth-order fine-structure parameter, which is small. The expression $|\langle M | S_+ + S_- | M' \rangle|^2$ is the same for all the allowed and forbidden hyperfine transitions of a given $M \rightarrow M'$ fine-structure transition and shows a weak angular dependence.

The expression for the angle between the effective magnetic fields $H_{\text{eff}}^{1/2}$ and $H_{\text{eff}}^{-1/2}$ is given by

$$\mu = \cos(H_{\text{eff}}^{1/2}, H_{\text{eff}}^{-1/2}) = 1 - 8 \frac{A^2 + B^2 - K^2}{K^2} \left(4 \frac{D}{H} \sin 2\beta - \frac{5}{6} \frac{1}{H} [(a - F) \sin 2\beta (3 - 7 \cos^2 \beta) + 2 \sqrt{2} a (4 \cos^4 \beta - 5 \cos^2 \beta - 1) \cos 3\varphi] \right)$$

$$-5 \cos^2\beta + 1) \cos 3\phi] \Big)^2 - 400 \frac{B^2 A^2}{K^2 H^2} \cos^2\beta \sin^4\beta \sin^2 3\phi. \quad (11)$$

Although μ shows a relatively weak orientation dependence, the fact that the functions $|d_{mm'}^{(I)}(\mu)|^2$ depend strongly on μ leads to a pronounced angular dependence of the transition probability. For the same reason, we included in Eq. (11) the effect of the fourth-order terms in the fine structure. In our case the effect of these terms is relatively small and μ shows mainly a $\sin^2 2\beta$ dependence. In other cases, e.g., Mn^{2+} in CdCO_3 ¹² where $D = 1.4$ G and $F = 8.75$ G, and Mn^{2+} in ZnCO_3 ¹³ where $D = 41.4$ G and $a - F = 11.4$ G, the effect of the fourth-order parameters in Eq. (11) can lead to an angular dependence of μ different from $\sin^2 2\beta$.

The expressions of the $|d_{mm'}^{(5/2)}(\mu)|^2$ functions, useful in our calculation, are given in Table I. The other $d_{mm'}^{(5/2)}(\theta)$ can be computed from these with the help of symmetry relations.¹⁴

Using this method, the ratio of the various forbidden transitions intensities to the allowed transition intensity is

$$\frac{P |M-1, m'\rangle \leftrightarrow |M, m\rangle}{P |M-1, m''\rangle \leftrightarrow |M, m''\rangle} = \frac{|d_{mm'}^{(I)}(\mu)|^2}{|d_{mm''}^{(I)}(\mu)|^2}. \quad (12)$$

The method of the effective electron magnetic field permits an accurate theoretical treatment of the EPR line intensity, without any limitation concerning the values of the fine-structure parameters. We note that in our derivation of $\cos(H_{\text{eff}}^{1/2}, H_{\text{eff}}^{-1/2})$ in Eq. (11) we used the electronic wave functions computed with the help of first-order perturbation theory. In the case of very large D parameters, either a higher approximation of the perturbation theory or a computation of the wave function by the diagonalization of the 6×6 matrix of the electronic Zeeman and fine-structure terms would be required. It must also be noted that a series expansion of the expressions for the transition probabilities obtained by the effective field method leads to the same expressions as obtained by perturbation theory, provided that an appropriate approximation is taken into account.

Table II contains a comparison of the experimental and computed line intensities for some of the transitions observed in the central fine-structure component of Mn^{2+} in calcite. We note that

the ratio of the forbidden transitions intensities to the allowed transitions intensities does not agree well with the predictions of Bleaney and Rubins's formula.¹⁵

CONCLUSION

We have observed the forbidden hyperfine transitions up to $\Delta m = \pm 5$ in the central fine component of the EPR spectrum of Mn^{2+} in calcite. The very low intensity of the high-order transitions explains why these transitions were not observed previously. We have obtained expressions for the line intensities which describe very well the experimental data.

The appearance of an additional splitting of the allowed and forbidden transitions in the central fine-structure component shows that in the calculation of the line positions, terms of order H^{-2} must be taken into account.

APPENDIX

The spin Hamiltonian (1) has been deduced as follows. We started with the spin Hamiltonian given by Bleaney and Trenam for the $^6\text{S}_{5/2}$ ions in axially distorted crystalline fields¹⁶:

$$\begin{aligned} \mathcal{H} = & g_{\parallel} \mu_B H_z S_z + g_{\perp} \mu_B (H_x S_x + H_y S_y) + A S_z I_z \\ & + B(S_x I_x + S_y I_y) + \frac{1}{3} D O_2^0 + \frac{1}{180} F O_4^0 + \frac{1}{180} a [O_4^0 + 5 O_4^4] \\ & + Q [I_z^2 - \frac{1}{3} I(I+1)] - \gamma \beta_N \vec{H} \cdot \vec{I}. \quad (A1) \end{aligned}$$

The primed O_n^m operators refer to the $\xi\eta\zeta$ axes, directed along the cube edges, and those without prime superscript refer to the xyz axes, with z directed along the distortion axis (in our case, one of the $\langle 111 \rangle$ directions in the $\xi\eta\zeta$ reference frame).

The primed operators are rewritten in the (xyz) frame and then the spin Hamiltonian is rewritten in a reference system, in which the electron Zeeman term, which in our case is much larger than the other terms, becomes diagonal.

By performing an Eulerian rotation $(\alpha\beta\gamma)$ of the reference frame, the spin operators O_n^m transform into a linear combination of spin operators $O_n^{m'}$ written in the new reference frame. Thus we have

$$\begin{aligned} O_n^m \rightarrow & \frac{E_n^m}{E_n^0} d_{0m}^{(n)}(\beta) \cos m\alpha O_n^0 + \sum_{m'' > 0} \frac{E_n^m}{E_n^{m''}} \{ [d_{m''m}^{(n)}(\beta) \cos(m'\gamma + m\alpha) + (-1)^m d_{m''-m}^{(n)}(\beta) \cos(m'\gamma - m\alpha)] O_n^{m''} \\ & - [d_{m''m}^{(n)}(\beta) \sin(m'\gamma + m\alpha) + (-1)^m d_{m''-m}^{(n)}(\beta) \sin(m'\gamma - m\alpha)] O_n^{m''*} \}, \quad (A2) \end{aligned}$$

$$\begin{aligned} O_n^{m*} \rightarrow & \frac{E_n^m}{E_n^0} d_{0m}^{(n)}(\beta) \sin m\alpha O_n^0 + \sum_{m'' > 0} \frac{E_n^m}{E_n^{m''}} \{ [d_{m''m}^{(n)}(\beta) \cos(m'\gamma + m\alpha) - (-1)^m d_{m''-m}^{(n)}(\beta) \cos(m'\gamma - m\alpha)] O_n^{m''*} \\ & + [d_{m''m}^{(n)}(\beta) \sin(m'\gamma + m\alpha) - (-1)^m d_{m''-m}^{(n)}(\beta) \sin(m'\gamma - m\alpha)] O_n^{m''} \}, \quad (A3) \end{aligned}$$

TABLE I. Expressions of some $|d_{mm'}^{(5/2)}(\mu)|^2$ useful in the calculation of the transition probabilities.

m	m'	$ d_{mm'}^{(5/2)}(\mu) ^2$
$\frac{5}{2}$	$\frac{5}{2}$	$\frac{1}{32}(1+\mu)^5$
	$\frac{3}{2}$	$\frac{5}{32}(1+\mu)^4(1-\mu)^2$
	$\frac{1}{2}$	$\frac{5}{16}(1+\mu)^3(1-\mu)^2$
	$-\frac{1}{2}$	$\frac{5}{16}(1+\mu)^2(1-\mu)^3$
	$-\frac{3}{2}$	$\frac{5}{32}(1-\mu)^4(1+\mu)$
	$-\frac{5}{2}$	$\frac{1}{32}(1-\mu)^5$
$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{32}(5\mu-3)^2(1+\mu)^3$
	$-\frac{1}{2}$	$\frac{1}{32}(1-\mu)(1+\mu)^2(5\mu-1)^2$
	$-\frac{3}{2}$	$\frac{1}{32}(1+\mu)(1-\mu)^2(5\mu+1)^2$
	$\frac{3}{2}$	$\frac{1}{32}(5\mu+3)^2(1-\mu)^3$
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{8}(5\mu^2-2\mu-1)^2(1+\mu)$
	$-\frac{1}{2}$	$\frac{1}{8}(5\mu^2+2\mu-1)^2(1-\mu)$

where E_n^m are numerical coefficients connected with the numerical factors of the Legendre polynomials:

$$E^0 = 8 \frac{\sqrt{\pi}}{3}, \quad E^1 = \frac{4}{\sqrt{5}} \frac{\sqrt{\pi}}{3}, \quad E^2 = \frac{8}{\sqrt{10}} \frac{\sqrt{\pi}}{3},$$

$$E^3 = \frac{4}{\sqrt{35}} \frac{\sqrt{\pi}}{3}, \quad E^4 = \frac{10}{\sqrt{70}} \frac{\sqrt{\pi}}{3}.$$

The spin operators O_n^m are given in several places (e.g., in Ref. 9 and 17). We reproduce here only the less common operators O_4^{1*} and O_4^{2*} :

$$O_4^{1*} \equiv -i \frac{1}{4} \{ [7S_z^3 - 3S(S+1)S_z - S_z](S_+ - S_-) \\ + (S_+ - S_-)[7S_z^3 - 3S(S+1)S_z - S_z] \}$$

$$O_4^{2*} \equiv -i \frac{1}{4} \{ [7S_z^2 - S(S+1) - 5](S_+^2 - S_-^2) \\ + (S_+^2 - S_-^2)[7S_z^2 - S(S+1) - 5] \}.$$

Of these two, O_4^{1*} is particularly useful in the computation of the transition probabilities for the hyperfine components of the $\Delta M = \pm 1$ fine transitions.

The $d_{m'm}^{(n)}(\beta)$ used here are the same as defined

TABLE II. Intensities of the various hyperfine transitions in the central fine-structure component at an orientation $\theta = 45^\circ$. The theoretical values have been obtained by the effective-field method. The intensity of the allowed hyperfine transitions at $\theta = 0^\circ$ was taken as equal to one.

Type of transition	m	m'	Intensity	
			Experimental	Theoretical
$\Delta M = \pm 1, \Delta m = 0$	$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$	$\frac{5}{2}$	0.80	0.766
			0.57	0.469
			0.41	0.358
$\Delta M = \pm 1, \Delta m = \pm 1$	$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$	$\frac{3}{2}$	0.21	0.206
			0.26	0.271
			0.29	0.296
$\Delta M = \pm 1, \Delta m = \pm 2$	$\frac{5}{2}$ $\frac{3}{2}$	$\frac{1}{2}$	20×10^{-3}	22.1×10^{-3}
			39×10^{-3}	37.1×10^{-3}
$\Delta M = \pm 1, \Delta m = \pm 3$	$\frac{5}{2}$ $\frac{3}{2}$	$-\frac{1}{2}$	10×10^{-4}	12×10^{-4}
			19×10^{-4}	18.6×10^{-4}
$\Delta M = \pm 1, \Delta m = \pm 4$	$\frac{5}{2}$	$-\frac{3}{2}$	35×10^{-6}	32×10^{-6}
$\Delta M = \pm 1, \Delta m = \pm 5$	$\frac{5}{2}$	$-\frac{5}{2}$	about	34.5×10^{-8}
			35×10^{-8}	

by Rose¹⁴ and relation (A2) given here is the same as relation (10) given in our paper,⁹ after taking into account that the $d_{m'm}^{(n)}(\beta)$ used here are related to those used in Ref. 9 by a factor of $(-1)^{m'}$.

The nuclear spin operators are then transcribed in a new coordinate system, in which the part of the hyperfine interaction which contains S_z becomes also diagonal in I .

In the case of the calcite crystal which has two magnetic complexes in the unit cell, related to each other by a rotation through α in the azimuthal plane, the spin Hamiltonian of Eq. (1) can be rewritten in a "crystal" system by performing a rotation $\frac{1}{2}\alpha$ in the azimuthal plane for one complex, and $(-\frac{1}{2}\alpha)$ for the other.

Note added in manuscript. After this work was performed, a rather simple treatment of the transition probabilities for the forbidden transitions $\Delta M = \pm 1, \Delta m = \pm 1$ and $\Delta M = \pm 2, \Delta m = 0$ in parallel and perpendicular configurations was published.¹⁸ We note that a study of the transition probabilities for the allowed and forbidden transitions for Mn^{2+} in calcite in variable field configurations was given by us (see Ref. 19).

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†Permanent address: Institute of Atomic Physics, Bucharest, Romania.

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z^3 Corrections to Energy Loss and Range*

J. D. Jackson

*Department of Physics and Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720*

and

R. L. McCarthy[†]

Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637

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Higher-order corrections to the stopping power proportional to z^3 are evaluated. Both close and distant collisions are considered. The energy-loss formula can be written $dE/dx = z^2 I + z^3(J_c + J_d)$, where I is the customary lowest-order energy loss and J_c and J_d are the close- and distant-collision parts of the z^3 term, respectively. The close-collision contribution J_c is a relativistic effect, first estimated in unpublished work by Fermi. It has the simple form $J_c = \pi\alpha C/2\beta$, where C is the standard constant multiplying β^{-2} times the Bethe-Bloch logarithm in I and α is the fine-structure constant. At high energies J_c gives a constant- z^3 contribution to the energy loss and causes a range difference ΔR roughly proportional to the range R for stopping particles of the same mass and energy, but opposite charge. For $2 < P/Mc < 20$, $\Delta R/R$ changes by less than $\pm 6\%$ and depends only slightly on the stopping material, varying from 1.9×10^{-3} for carbon to 2.5×10^{-3} for lead for $z = \pm 1$. The distant-collision effect is important only at low velocities. The calculation of this contribution is patterned after a recent work of Ashley, Ritchie, and Brandt, but differs from it in detail. Using a statistical model for the atom it is found that at low velocities the relative z^3 contribution can be written $J_d/I = F(V)/(Z)^{1/2}$, where Z is the atomic number of the stopping medium and $F(V)$ is a universal function of the reduced velocity variable $V = 137\gamma\beta/(Z)^{1/2}$. In the region where J_d/I is appreciable ($1 < V < 10$), $F(V)$ varies as V^{-n} with $n \approx 2.0-2.5$. These results on the z^3 effect at low velocities are in good agreement with available data on comparison of the energy loss of helium ions and protons of the same velocities. Range differences are calculated for carbon, copper, lead, and emulsion absorbers, including the effects of both close and distant collisions. The results are in rough agreement with data on slow-stopping pions and Σ hyperons in emulsions and in good agreement with very recent measurements of fast positive and negative muons. The upper limit of the range of validity of the results is examined in some detail. It is found that the approximations begin to fail for dynamic reasons above $\gamma \approx 20$ for muons, and presumably also for other heavy particles.

I. INTRODUCTION

For a heavy particle of charge ze and velocity $v = \beta c$ passing through a medium of atomic number Z , the standard expression for energy loss in $\text{MeV cm}^2/\text{g}$ is¹⁻³

$$\frac{dE}{dx} = z^2 I = C \frac{z^2}{\beta^2} L(\beta, Z), \quad (1)$$

where

$$C = \frac{4\pi N_0 e^4}{mc^2} \frac{Z}{A} = 0.307 \frac{Z}{A} \quad (2)$$

and $L(\beta, Z)$ is given at velocities well above the orbital velocities of the atomic electrons by

$$L(\beta, Z) \approx \ln\left(\frac{2\gamma^2 mv^2}{I_0 Z}\right) - \beta^2. \quad (3)$$

The parameter I_0 characterizes the medium; empirically it varies somewhat over the Periodic