FINE STRUCTURE AND HYPERFINE STRUCTURE OF PARAMAGNETIC RESONANCE OF Cr^{+++} *IN SYNTHETIC RUBY*

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THE electronic paramagnetic resonance spectrum for the Cr^{+++} ion in synthetic ruby (Al_2O_3) has been investigated earlier at 9000 and 12000 Mcs.[1-3] We have carried out a more complete investigation of this spectrum at 37,860 Mcs.

In the synthetic ruby crystal the Cr^{+++} ion (ground state ^4F, and spin $S = 3/2$) is in an electric field of trigonal symmetry. This field splits the lowest electrical level of the ion into two sublevels which are separated by 0.38 cm^{-1}. The behavior of the electrical levels in the presence of an external magnetic field is given by the spin Hamiltonian[4]

$$\mathscr{H} = D\,[S_z^2 - {}^1/_3 S(S+1)] + g_{\parallel}\beta H_z S_z$$
$$+ g_{\perp}\beta (H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y).$$

The fine structure was studied in a synthetic-ruby single crystal with a chromium dilution of 1:1,000. The lines were measured at two orientations of the crystal in the external magnetic field: (1) with the trigonal axis $Z \parallel H$, and (2) with the trigonal axis $Z \perp H$.

In the first case three absorption lines were observed; these correspond to transitions between levels with the following values of M_Z:

$$1)\ -{}^3/_2 \leftrightarrow -{}^1/_2, \quad 2)\ -{}^1/_2 \leftrightarrow +{}^1/_2, \quad 3)\ +{}^1/_2 \leftrightarrow +{}^3/_2.$$

In the second case the energy states ϵ_1, ϵ_2, ϵ_3, and ϵ_4 are a mixture of states with different M_Z. In all, six absorption lines were observed; the first three lines have intensities two orders of magnitude smaller than the other three.

The constants in the spin Hamiltonian determined from the lines were as follows:

$$D = -0.1912 \pm 0.0010\,\text{cm}^{-1}; \quad g_{\parallel} = 1.982 \pm 0.002;$$
$$g_{\perp} = 1.979 \pm 0.009.$$

The positions of all lines were calculated using these values. The agreement between the experimental values and the calculated values is good (cf. table). The sign of D is determined from a measurement of the relative line intensities at T = 4.2° K. We may note that at this temperature it is easy to saturate the lines. An estimate of the spin-lattice relaxation time T_1 indicates that this quantity is of the order of 10^{-2} sec.

Transition	H_{exp}, Oersted	H_{cal}, Oersted
Parallel orientation		
$-{}^3/_2 \longleftrightarrow -{}^1/_2$	9510	9510
$-{}^1/_2 \longleftrightarrow +{}^1/_2$	13650	13650
$+{}^1/_2 \longleftrightarrow +{}^3/_2$	—	17790
Perpendicular orientation		
$\varepsilon_1 \longleftrightarrow \varepsilon_4$	4293	4296
$\varepsilon_3 \longleftrightarrow \varepsilon_4$	5553	5557
$\varepsilon_1 \longleftrightarrow \varepsilon_2$	7620	7627
$\varepsilon_2 \longleftrightarrow \varepsilon_4$	11595	11595
$\varepsilon_3 \longleftrightarrow \varepsilon_2$	13400	13398
$\varepsilon_1 \longleftrightarrow \varepsilon_3$	15710	15697

The hyperfine structure was investigated in a sample containing 95 per cent of the Cr^{53} isotope; the dilution was 1:10,000. The hyperfine structure was resolved only for the $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$ line in the parallel orientation and the $\epsilon_2 \longleftrightarrow \epsilon_3$ line in the perpendicular orientation. There are four components, corresponding to the different projections of the nuclear spin ($I = 3/2$). The components are not equally spaced; the distance between the two inner lines is less than one-third of the distance between the outer lines. The unequal spacing may be attributed to a weak line at the center of the spectrum, due to the even chromium isotope in the sample.

The fine-structure splitting constants A and B were determined:

$$|A| = (16.8 \pm 0.04) \cdot 10^{-4}\text{cm}^{-1};$$
$$|B| = (16.8 \pm 0.06) \cdot 10^{-4}\text{cm}^{-1}$$

The fact that these values are the same indicates that the hyperfine structure is essentially isotropic.

The values found in the present work for the constants in the spin Hamiltonian for Cr^{+++} in a synthetic ruby single-crystal are in good agreement with the values reported in Refs. 1—3.

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ENERGY SPECTRUM OF ELECTRONS IN OPEN PERIODIC TRAJECTORIES

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In Ref. 1 we have given the equation of motion for an electron which obeys the dispersion relation $E(\mathbf{k}) = \Sigma A_n e^{i\mathbf{kn}}$ in a magnetic field $(H = H_z)$:

$$\sum_{\mathbf{n}} A_{\mathbf{n}} \exp\left\{i\ (k_2 n_2 + k_3 n_3) - i\frac{n_1 n_2}{2\alpha_0^2}\right\} f\left(k_2 - \frac{n_1}{\alpha_0^2}\right) = Ef(k_2). \qquad (1)$$

It is assumed that $\epsilon = \sqrt{a_1 a_2}/\alpha_0 \ll 1$ $(\alpha_0^2 = \hbar \times c/eH$; the a_i are the lattice constants). In Ref. 2 solutions of this equation were investigated for open periodic trajectories. In the present note we verify the assertion made in Ref. 2 concerning the exponential smallness of the breaks in the continuous energy spectrum in the case in which the function $\kappa_1 = \kappa_1(k_2)$ (the equation of the trajectory, i.e., the intersections of the surface $E(\mathbf{k}) = \text{const.}$ with the plane $k_3 = \text{const.}$) is analytic.

It will be assumed that κ_1 is large enough everywhere (the other cases are considered in Ref. 2) so that the quasi-classical approximation can be used, that is, we write

$$f(k_2) = \exp\left\{\frac{i}{\varepsilon^2}\varphi_1 + \varphi_2 + \frac{\varepsilon^2}{i}\varphi_3 + \left(\frac{\varepsilon^2}{i}\right)^2 \varphi_4 + \cdots\right\}. \qquad (2)$$

Solution of this equation is much more difficult than solution of the Schrödinger equation because Eq. (1) is a difference rather than a differential equation. However, the general properties of the solution are the same in both cases. The following expressions are obtained in the first four approximations:

$$\varphi_1 = -\int \varkappa_1 dx; \qquad \varphi_2 = -{}^1/_2 \ln P;$$

$$\varphi_3 = \int\left\{-\left(\frac{P'Q}{P}\right)'\frac{1}{4P} + \frac{QP'^2}{8P^3} + \frac{Q''}{8P} + \frac{R\varkappa_1''}{24P}\right\}dx;$$

$$\varphi_4 = \frac{\varphi_3' Q}{2P} - \frac{1}{24P}\left\{6R(\varphi_2'^2 + \varphi_2'') + 3R'\varphi_2' + 3RP'\varphi_2' P^{-1} - 3R\varphi_2'' + \frac{1}{2}R'' + \frac{1}{2}\frac{R'P'}{P} + \frac{RP'^2}{P^2} - \frac{RP''}{2P}\right\}. \qquad (3)$$

Here we have introduced the notation

$$P = \partial E/\partial\varkappa_1, \quad Q = \partial^2 E/\partial\varkappa_1^2, \quad R = \partial^3 E/\partial\varkappa_1^3, \qquad (4)$$

where κ_1 and k_2 are measured in dimensionless units (by κ_1 we are to understand $\kappa_1 a_1$ and by x we are to understand $k_2 a_2$).

Just as in the Schrödinger equation, the quantities φ_{2n}' are total derivatives and since P, Q, R, are periodic in k_2, this same property is characteristic of the even approximations φ_2, φ_4, ... Consequently, if Eq. (2) is written in the form

$$f(k_2) = \rho e^{i\varphi}, \qquad (5)$$

the modulus ρ will be a periodic function of k_2 (while the phase φ is an integral of a periodic function and does not change sign).

When displaced by one period, (5) should be multiplied by e^{ip}, where e^{ip} is ± 1 at the boundary of the allowed energy intervals. This locates the discontinuity at once. Keeping the first two approximations φ_1 and φ_2 (corresponding to the usual quasi-classical analysis), we have:

$$f(k_2) = P^{-1/2}\exp\left\{-i\varepsilon^{-2}\int_0^x \varkappa_1 dx\right\}.$$

The condition $e^{ip} = \pm 1 = e^{i\pi n}$ obviously means:

$$S = 2\pi\alpha_0^{-2} n \qquad (6)$$

[S is the area bounded by the curve $\kappa_1(k_2)$ in one cell]. Thus the center of the allowed interval is determined from the same relation that applies for the discrete levels in the case of closed trajectories:

$$S = 2\pi\alpha_0^{-2}(n + {}^1/_2). \qquad (7)$$

The width of the discontinuities can be determined from the usual dispersion equation:

$$\cos p = \frac{f(2\pi/a_2) + f(-2\pi/a_2)}{2f(0)}, \qquad (8)$$

which follows from the relation $f(k_2 \pm 2\pi/a_2) = e^{ip} f(k_2)$. Since ρ the modulus of the function in Eq. (5) is periodic, Eq. (8) is of the form

$$\cos p = \cos\{\varepsilon^{-2}\varphi_1(2\pi/a_2) - \varepsilon^2\varphi_3(2\pi/a_2) + \varepsilon^6\varphi_5(2\pi/a_2) - \ldots\}. \qquad (9)$$

This equation can always be solved. It shows that the discontinuities fall off with ϵ faster than any finite power of ϵ. The results of Ref. 2 and the well-known fact that in the discontinuities in the