(b) Supposing $i\hbar\dot{\psi} = H(t)\psi$ to be solved, let F_X be computed and compared with $M\ddot{X}$, an unsatisfactory comparison leading to the next approximation $M\ddot{X}_2 = F_{X_1}$, etc. In the case that the nuclear motion corresponds to a collision, as in atom-atom collisions, the initial state $\psi(x,-\infty)$ for step (b) is well defined; for bound nuclear motions it is not clear how to specify an initial state in general, though in special cases the periodicity and turning points of the classical motion may serve to fix $\psi(x,t)$ uniquely. As for the nonstationary states themselves, one can appeal to an expansion of $\psi(x,t)$ in instantaneous eigenfunctions, $\psi = \sum f_n(t)\phi_n(x,t)$ with $H(t)\phi_n(x,t) = E_n(t)\phi_n$. The $\phi_n(x,t)$ are of course closely related to the starting functions $\omega_n(x,X)$ of the Born-Oppenheimer approximation method, $H'\omega_n = \epsilon_n(X)\omega_n$, $(H' \equiv H - T_X)$ in which at first the nuclear kinetic energy is disregarded and X is a numerical parameter. It is interesting to see, however, that in the present scheme, in contrast to the Born-Oppenheimer scheme, the nuclear kinetic energy is at the outset taken into consideration, and that the expansion in time-frozen eigenfunctions is fundamentally simpler than the Born-Oppenheimer expansion $\sum U_n(X)\omega_n(x,X)$ in space-frozen eigenfunctions [first-order ordinary differential equations for $f_n(t)$, second-order partial differential equations for $U_n(X)$].

What has been done in the formulation of Eq. (1) is to break up the conservative motion of the whole molecular system into two individually nonconservative parts. This is but an essential cost of attempting to survey one of the parts, the nuclear motion, in abstraction from the rest, and emphasizes that no conservative view of the nuclear motion can wholly suffice for its description. The view supplied by the dynamical Feynman theorem should be capable in relatively simple fashion of accounting accurately, if only classically, for the "kinetic energy corrections" as a whole that arise from the billowing tides of electrons that are themselves induced by the rushing nuclei. The next step of quantization of the classical motion can be considered only after this motion is more fully understood. In a later report it is hoped to elaborate some of the points made here through a discussion of H_2^+.

*Consultant, Aerodynamics Research Department. Permanent address, Physics Department, University of Buffalo, Buffalo, New York.

[1]R. P. Feynman, Phys. Rev. 56, 340 (1939).
[2]M. Born and R. Oppenheimer, Ann. Physik 84, 457 (1927).

FINE STRUCTURE, HYPERFINE STRUCTURE, AND RELAXATION TIMES OF Cr3+ IN TiO2 (RUTILE)*

H. J. Gerritsen, S. E. Harrison,
H. R. Lewis, and J. P. Wittke
RCA Laboratories, Princeton, New Jersey
(Received January 20, 1959)

We have studied the paramagnetic spectrum of a single crystal of TiO2 (rutile) in which 0.12% of the Ti ions were replaced by Cr ions. The resonances observed at 23 800 Mc/sec and 9520 Mc/sec are shown as a function of field and crystal orientation in Figs. 1 and 2. All of these points, with the exception of those which are denoted by cross marks, are attributed to Cr3+ ions which have replaced titanium ions in the crystal. The resonances not believed due to Cr have an intensity of about 1% of that of the Cr lines and are thought to be due to another paramagnetic impurity. Chemical analysis showed that Fe and Cu are indeed present in concentrations of 3-30 parts per million.

The rutile form of TiO2 is a tetragonal crystal belonging to the class D_{4h}.[1] There are two Ti4+ ions in a unit cell and each of these has six
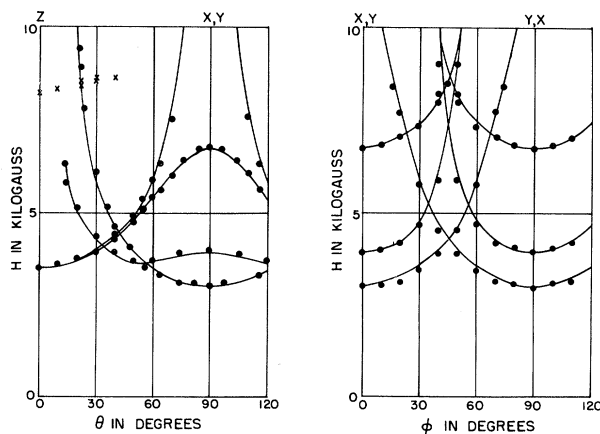

FIG. 1. The points shown in the figures are the observed resonances at 23 800 Mc/sec. The solid lines give the theoretical resonance fields for the parameters stated in the text.
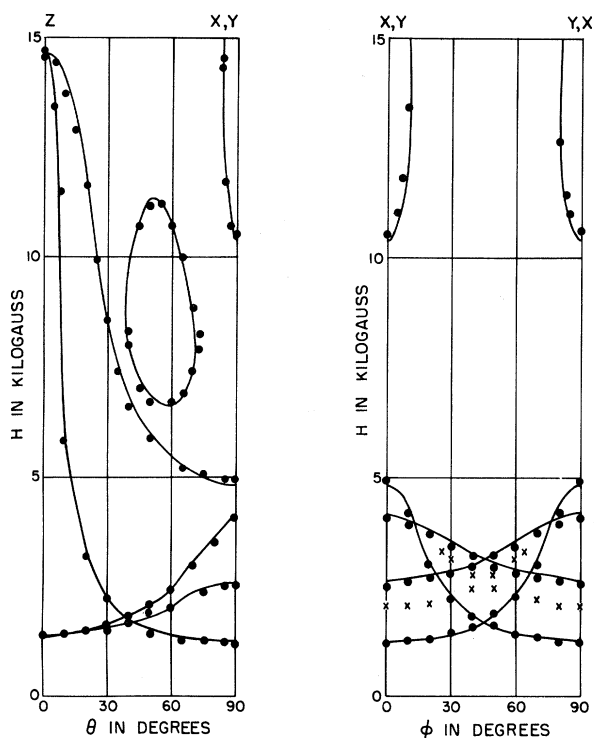
FIG. 2. The points shown in the figures are the observed resonances at 9520 Mc/sec. The solid lines give the theoretical resonance fields for the parameters stated in the text.

$\odot = Ti^{4+}$ OR Cr^{3+} IONS

$\odot = O^{2-}$ IONS

FIG. 3. Crystal structure of TiO_2 and magnetic axes. $\angle APE = \angle BPE = 90° = \angle A'QE' = \angle B' QE'$. $\angle APB = \angle A'QB' = 78°$. $EP = E'Q = 1.99A$. $AP = BP = 1.89A = A'Q = B'Q$.

$$0 = W^4 - W^2 \left(\tfrac{5}{2}h^2 + 2D^2 + 6E^2\right)$$
$$+ Wh^2 \left(2D - 6D\cos^2\theta - 6E\sin^2\theta\,\cos2\phi\right)$$
$$+ \tfrac{9}{16}h^4 + \tfrac{1}{2}h^2 \left(D^2 - 6D^2\cos^2\theta + 9E^2\cos2\theta\right)$$
$$+ 12DE\sin^2\theta\,\cos2\phi) + (D^2 + 3E^2)^2.$$

The symbols are: W = energy, $h = g\beta H$, θ = angle between z axis and magnetic field, and ϕ = angle between x axis and projection of magnetic field in the xy plane.

Values of observed line widths and resonant fields along the symmetry axes are given in Table I. These measurements were made at room temperature. A rough check at 78° and 4.2°K indicates that any shift in resonant fields with reduced temperature is not greater than 1%.

Relaxation times measured using conventional

neighboring oxygen atoms which produce an orthorhombic field at the position of the titanium ion. The symmetry of the Ti^{4+} ion and the ligating oxygens is D_{2h}. The z axis is parallel to the c axis, while the magnetic x and y axes are parallel to the 110 and 1$\bar{1}$0 directions. The positions of the oxygen ions around two nonequivalent titanium ions differ from one another by a rotation through 90° around the c axis. (See Fig. 3.) As a result the paramagnetic spectrum has a period of 90° when rotated around the tetragonal crystal axis.

The four lowest electronic levels of a Cr^{3+} ion which has replaced a Ti^{4+} ion in rutile are described by a spin-Hamiltonian[2] of the form

$$H = \beta g \vec{H} \cdot \vec{S} + D\left[S_z^2 - \tfrac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2). \quad (1)$$

We are able to fit the observed resonances in the zx, zy, and xy planes to those predicted by Eq. (1) if we assume

$$g = 1.97, \quad D = 0.55 \text{ cm}^{-1}, \quad E = 0.27 \text{ cm}^{-1}.$$

The calculation of the energy levels was done by machine computation for which purpose the secular determinant was developed in the form
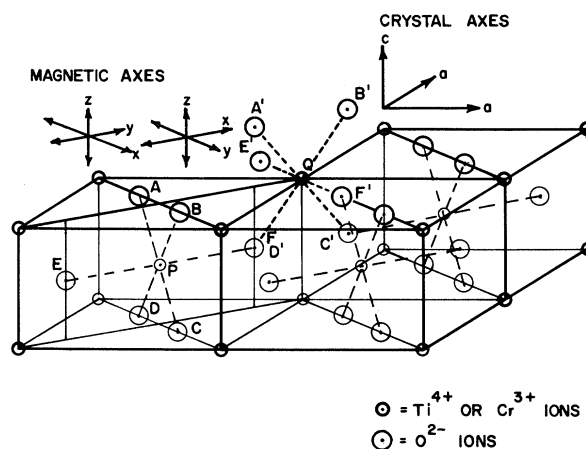
Table I. Resonant fields and line widths of Cr in TiO_2.

Transition		Axis	Frequency (kMc/sec)	Resonant field	Line width (gauss)
1/2	3/2	z	9.520	1390	12
1/2	3/2	z	23.79	3505	9
-3/2	-1/2	z	9.520	14800	
-3/2	-1/2	y	9.520	1200	21
-3/2	-1/2	y	23.79	3010	7
-1/2	3/2	y	23.79	3960	35
3/2	1/2	y	9.520	4065	21
3/2	1/2	y	9.520	10600	
1/2	3/2	x	9.520	2560	17
1/2	3/2	x	23.79	6750	23
-3/2	-1/2	x	9.520	4940	29

Table II. Relaxation times of Cr in TiO_2.[a]

Transition		Axis	Frequency (kMc/sec)	Resonant field (gauss)	Temp. (°K)	T_2(sec)	T_1(sec)
1/2	3/2	z	23.79	3505	78	5.3×10^{-9}	4×10^{-4}
1/2	3/2	z	23.79	3505	4.2	5.3×10^{-9}	4×10^{-2}
1/2	3/2	x	23.79	6750	4.2	4.9×10^{-9}	5×10^{-2}

[a]The conversion factor needed to go from linewidth to T_2 is obtained by using the slope of the calculated curves for energy level vs magnetic field.

c.w. methods[3] are given in Table II. These are order-of-magnitude estimates; the large possible error arises almost entirely from uncertainty about the radio-frequency field distribution within the cavity. The dielectric constant of TiO_2 is very large, anisotropic, and temperature-dependent. Thus, mode distortion in the cavity due to the sample is difficult to estimate and further study will be required to fix more accurately the values of T_1.

Because some of the resonance lines are very narrow, the four-line hyperfine structure due to Cr^{53} (9.55% of natural Cr) is easily observed. The hyperfine splitting is described by adding to the spin-Hamiltonian terms of the form $A_z I_z S_z + A_x I_x S_x + A_y I_y S_y$.

A splitting of 50 gauss between the outer of the four hyperfine lines was observed along all three axes and at both frequencies used. One can show theoretically that the over-all splitting measured in this way is equal to $3A/g\beta$ independent of D, E or H, as long as these are large compared to A. The observed splittings of 50 gauss show that $A_x = A_y = A_z = 0.0015$ cm^{-1}. This is in good agreement with measurements on other Cr-doped crystals[4] and a further support of the theory of configurational interaction. Because the inner hyperfine lines were not completely separated from the strong resonance due to the Cr^{52}, it was not possible to detect quadrupole effects. The distances between the four hyperfine lines were equal to within 10%.

The narrow lines and long relaxation times of Cr^{3+} in TiO_2, together with the high dielectric constant and good mechanical properties of the crystal, indicate that it may be a very effective material for use in a solid-state maser. With 1 mw of power incident on a cavity with a Q of approximately 1000, we observed saturation parameters of about one at 78°K and 100 at 4.2°K. The

voltage reflection coefficient was about 0.5.

[1]R. W. C. Wyckoff, Crystal Structures Handbook (Interscience Publishers, Inc., New York, 1958).

[2]B. Bleaney and K. W. H. Stevens, Reports on Progress in Physics (The Physical Society, London, 1953), Vol. 16, p. 107.

[3]Bloembergen, Pound, and Purcell, Phys. Rev. 73, 679 (1948).

[4]K. D. Bowers and J. Owen, Reports on Progress in Physics (The Physical Society, London, 1955), Vol. 18, p. 304.

POLARIZATION OF FLUORESCENCE IN ZnS AND CdS SINGLE CRYSTALS

A. Lempicki
Research Laboratories,
Sylvania Electric Products Incorporated,
Bayside, New York

The polarization of impurity fluorescence has been observed in both ZnS and CdS crystals. The specimens were obtained by vapor phase growth and in the case of ZnS have been deliberately doped with Cu and Mn. Plate-like crystals with the c axis in the plane were used for the measurements.

The fluorescence was excited by filtered 3650A radiation incident perpendicularly to the plate surface. Natural or plane polarized radiation